THE CRYSTAL STRUCTURE OF PARA-NITRANILINE AND NAPHTHALENE

THESIS

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by

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PREFACE

The work on para-nitraniline described in this thesis has already been published conjointly with Professor J. Monteath Robertson, F.R.S. (Nature, 160, 569, 1947; Acta Crystallographica, 1, 252, 1948) and it has also been read before the First Congress of the International Union of Crystallography, Harvard University, in July 1948.

The first half of the experimental section of the work on naphthalene was carried out in collaboration with Dr. J. G. White (see page 112). The completed research into the crystal structure of this compound will be prepared for publication in due course, in conjunction with Dr. J. G. White and Professor J. Monteath Robertson.

I wish to offer my sincere thanks to Professor Robertson for suggesting the problems for research, and for his constant assistance and encouragement. I also wish to thank Dr. Howard T. Evans, Jr. of the Massachusetts Institute of Technology for the use of his precession camera; and am very grateful to the Department of Scientific and Industrial Research for a Maintenance Allowance.

November, 1948. S. C. A.

University of Glasgow.

SUMMARY

A quantitative x-ray investigation into the crystal and molecular structure of para-nitraniline, based on double Fourier series, and of naphthalene, based on triple Fourier series, has led to a complete determination of the atomic parameters.

In the former compound, the nitro-group is found to be symmetrical and to lie in the plane of the benzene ring. In addition to rather weak hydrogen bridges connecting the oxygen atoms of the nitro-groups to the nitrogen atoms of the amino-groups of adjacent molecules, there is a very close approach (2·7 - 3·0Å.) between one of the nitro-group oxygen atoms, and three of the aromatic carbon atoms of an adjoining molecule. This appears to be an intermolecular attraction of a new type, and one which may be responsible for the formation of the large class of molecular complexes between aromatic nitro-compounds and polycyclic aromatic hydrocarbons.

The atomic co-ordinates of naphthalene have been determined with great accuracy, and definite variations in bond length within the molecule have been observed. The shortest bond is in the chemically reactive " αβ" position, the central bond is the usual aromatic length, as is also the outermost linkage, and the remaining bond is somewhat longer than usual.

C O N T E N T S

INTRODUCTION

An early result of simple resonance theory was the postulation of equivalence in the two nitrogen-oxygen linkages of the nitro-group. Until that time, in the late 1920's, these bonds were regarded as consisting of one true double bond, and one co-ordinate bond, which would imply a measurable dipole moment and also a difference in bond lengths. An elegant demonstration of the equality of the linkages was the experimental determination of the dipole moment of para-dinitrobenzene (Tiganik, 1931), which proved to be very small, and until 1935, there was no further doubt about the symmetry of the nitro-group. In that year, the now classically controversial paper of James, King and Horrocks appeared on para-dinitrobenzene, in which the nitrogen-oxygen distances were reported to be 1.25 and 1·10Å.

This was the first of a number of investigations into the structure of the nitro-group by x-ray methods, and a certain amount of disagreement among their results soon became apparent. Two main schools of thought emerged, one in which the nitro-group appeared to be non-symmetrical, and the other in which it was held to be in strict accord with the resonance viewpoint. There have not been suffic-

ient investigations so far to permit any final decision on the problem to be made on a statistical basis, and it thus becomes necessary to examine the existing work carefully, on its merits.

The experimental results leading to a belief in the non-symmetrical nitro-group were obtained by James, King and Horrocks and also by van Niekerk (1942) in 4-4' dinitro-diphenyl, in which compound he claimed nitrogen-oxygen distances of 1·41 and 1·21Å. In both papers, the limits of accuracy quoted were ±0·02Å. The symmetrical structure was advanced in the case of meta-dinitrobenzene, which was independently investigated in two laboratories (Archer, 1946; Gregory and Lasettre, 1947), where the distances given were 1·20 and 1·19Å. respectively, the limits quoted being ±0·03Å. in the latter instance, and not being given in the former.

The symmetrical structure was also put forward in a new paper on para-dinitrobenzene (Llewellyn, 1947) in which the distance was said to be 1·25±0·02Å. This work, however, may readily be shown not to be self-consistent. It was claimed that as the result of a three-dimensional Fourier analysis, the final atomic co-ordinates represented a symmetrical nitro-group, a symmetrical benzene ring, a collinearity between the two nitrogen atoms and the carbon atoms to which they are joined (N C C'N'), and also a

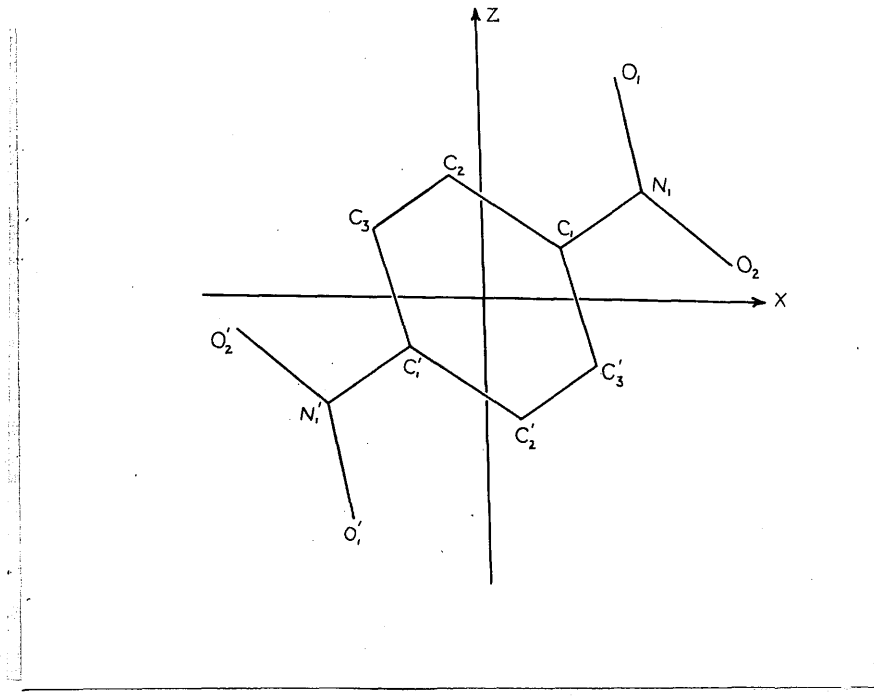


Fig. 1. Model of the para-dinitrobenzene molecule as observed along the b-axis.

coplanarity between the nitro-group and the benzene ring. The section given in this paper, parallel to (010), is such that $O_1 O_2$ and $C_2 C_3'$ (see Fig. 1.) are not parallel, as they are required to be geometrically, if these statements are to describe the structure accurately.

It is thus clear, from the published data, that one or a combination of several of the statements concerning the

symmetry of the nitro-group and the benzene ring, the collinearity of $N\,C\,C'N'$ or the coplanarity of the nitro-group and the aromatic ring cannot be correct. The interesting feature is that preliminary two-dimensional Fourier diagrams prepared by the present author (Abrahams and Robertson, 1947) for para-dinitrobenzene, on the basis of James, King and Horrocks' final co-ordinates and new experimental data, yielded the same non-parallelism of O_1O_2 and $C_2C'_3$, as did also, of course, the original diagram in 1935. It may thus be assumed that this effect is real, since it is shown by all three analyses.

Llewellyn's three-dimensional analysis is also open to further criticism. The intensities of all possible planes extending to the very edge of the reciprocal sphere have not been determined, resulting in an artificial termination of the triple Fourier series. Also, the intensities themselves were obtained by comparison between the reflected spots on the film and a set of calibrated spots produced by means of a collimated x-ray beam and a variable time factor. It seems likely that this technique will introduce a fairly large error into the intensity estimate, with a correspondingly higher random inaccuracy in the structure factors. Both these effects will limit the accuracy of the measured bond distances (Robertson and White, 1947a), as will also the method of computation, in

which the electron density all over the unit cell was not obtained, but only along a few selected lines and sections.

It may thus be seen that the problem of the crystal structure of para-dinitrobenzene may not yet be regarded as finally solved.

The only other x-ray investigations published so far on nitro-compounds are into ethylene dinitroamine Llewellyn and Whitmore, 1948) where nitrogen-oxygen distances are given as equal at 1·21Å, picryl iodide (Huse and Powell, 1940) and the molecular complex of 4-4' dinitro-diphenyl with 4-hydroxydiphenyl (Saunder,1946) and with benzidine, NN;N'N'-tetramethyl benzidine, 4-4' dihydroxy diphenyl, 4-iodo diphenyl and 4-bromo diphenyl (Saunder, 1947). The first of these papers has appeared too recently to allow a full assessment. The second has necessarily suffered some loss of accuracy due to the introduction of the heavy atom with its associated diffraction effects. In the other cases, the complexity of the structures investigated has made direct measurement of the nitrogen-oxygen distances impossible, and hence these researches do not make any direct contribution to the problem of the structure of the nitro-group, with the exception of the most recent work.

A little further data is also available, obtained by electron diffraction experiments on nitro-methane (Brockway, Beach and Pauling, 1935) and on tetra nitro-methane (Stosick, 1939). In both studies, the distance

of 1·23±0·02Å. was reported. The value of this evidence is somewhat doubtful, for in those cases where the molecule contains more than three or four atoms, the comparatively few experimental data obtained by this method does not permit of an unambiguous solution, and so the final bond distances are rendered somewhat inconclusive. It may thus be seen that the nitrogen-oxygen distance in the nitro-group lies between 1·1 and 1·2Å., but the precise value, and the question of possible symmetry in the group still remain in doubt. The values assigned to the oxygen-nitrogen-oxygen valency angle also show considerable variation, with 128° and 120° reported by Gregory and Lasettre, 130° by Archer, 116° 37' by van Niekerk and 124° by Llewellyn.

Another problem is in the determination of the distance from the nitrogen atom of the nitro-group to the adjacent carbon atom of the aromatic ring to which it is attached, where again, a multiplicity of results have been recorded. The values obtained are 1·53±0·02Å. (James, King and Horrocks, 1935), 1·56±0·02Å. (van Niekerk, 1942), 1·42 ±0·03Å. (Gregory and Lasettre, 1947), 1·53Å (Archer, 1946), 1·41±0·02Å. (Llewellyn, 1947), 1·46±0·02Å. (Brockway, Beach and Pauling, 1935) and 1·47±0·02Å. (Stosick, 1939). Distances of 1·41±0·03Å in trans-azobenzene (de Lange, Robertson and Woodward, 1939) and 1·45±0·04Å. in cis-

azobenzene (Robertson,1939) for a fairly similar carbon-nitrogen bond have also been recorded.

The corresponding distance between the nitrogen atom of an amino group and the adjacent carbon atom of an aromatic ring appears to have received little attention, apart from the values found in meta-tolidine hydrochloride (Hargreaves and Taylor, 1941) of 1·40 and 1·39Å. In the case, however, where the amine group is attached to an aliphatic carbon atom, a considerable number of results have been reported. In urea, the carbon-nitrogen distance is said to be 1·37Å. (Wyckoff and Corey, 1934), in glycine to be 1·39Å. (Albrecht and Corey, 1939), in dl-alanine to be 1·42Å. (Levy and Corey, 1941), in methyl ammonium chloride to be 1·47Å. (Hughes and Lipscomb, 1946), in geranylamine hydrochloride to be 1·49Å. (Jeffrey, 1945), in L-threonine to be 1·51Å. (Shoemaker, Schomaker, Nowacki, Donohue and Corey, 1948) and in glycyl glycine to be 1·48 and 1·51Å. (Hughes and Moore, 1948 and 1948). Also, in hexa-methylene diamine and its dihydrochloride and dihydrobromide (Robertson and Binnie, 1948) the distance is found to be 1·51±0·02Å. The nitrogen-carbon distance in the case of attachment to an aliphatic molecule, is not of course, necessarily the same as when attached to an aromatic molecule.

In the various investigations into the structure of

the nitro-group which have been quoted, a curious common feature soon revealed itself, when the agreement between observed and calculated structure factors was examined. If the measure of agreement is expressed by means of the relation

$$\Delta = \frac{\Sigma |F_{obs.} - F_{calc.}|}{\Sigma |F_{obs.}|}$$

Δ has the value 43% for para-dinitrobenzene (James, King and Horrocks, 1935). This figure is unduly large because the intensities were on an absolute scale and theoretical atomic scattering curves were employed, with the consequence that $\Sigma F_{obs.}$ was considerably smaller than $\Sigma F_{calc.}$ When the two sets of structure factors are placed upon the same scale, Δ drops to 35%. The structure factors for 4-4' dinitrodiphenyl were not given in the paper, and an attempt to obtain them by means of a personal communication received no answer, so that no appreciation of the value of this structure, based on the discrepancy, may be made. It may, however, be significant that the atoms in the (Okl) projection, which should all be clearly resolved, are not particularly round, and in one case, resolution has not been achieved, although the distance between atomic centres is about 0·85Å in projection.

In the case of meta-dinitrobenzene (Archer, 1946) the structure has a discrepancy of 27·5% and the other determination (Gregory and Lasettre, 1947) has the value of 32·8%.

The most recent structure of para-dinitrobenzene (Llewellyn, 1947) has $\Delta = 25{\cdot}5\%$. These figures refer to the (hk0) zone for the meta-compound and the (h0l) zone for the para-compound.

These discrepancies may be compared with 14% for coronene (Robertson and White, 1945) and 10% for oxalic acid (Dunitz and Robertson, 1947). In the case of the nitro-compounds, a somewhat higher discrepancy may be expected, for several reasons. Thus, three atomic scattering curves are required instead of only one or two, and this will add to the uncertainty in the calculated structure factor; more important, the usual form of the atomic scattering factor which is based upon the premise that the atom concerned is spherically symmetrical (James, Waller and Hartree, 1928) is probably not a sufficiently good approximation in the case where atoms are involved which have a considerable interaction upon each other. This is clearly the case in the nitro-group where it is most likely that the x-ray scattering is caused by the group as a whole, rather than by the individual atoms. If this is, in fact the case, it would effectively introduce an asymmetric element into the scattering function, so that it would be dependent not only upon $\frac{\sin\theta}{\lambda}$, but also upon the geometrical position of the associated plane in the unit cell.

A preliminary investigation into para-dinitrobenzene has shown that, using a composite empirical atomic scattering curve, and plotting (Fobs. - Fcalc.) with the appropriate sign, on the reciprocal lattice at the planes concerned, a definite pattern results when points of equal sign and magnitude are connected. The shape of this pattern coincides very nearly with those planes, parallel with the nitrogen-oxygen bonds in projection, which have the greatest discrepancies. Thus, in the nitro-compounds, it would almost certainly be more satisfactory if a standard atomic scattering curve were used for carbon, in conjunction with an empirical curve for nitrogen and oxygen, which would vary in such a way as to reduce this pattern to the minimum value. It seems likely that a similar effect to this operates in all cases involving atoms of widely differing electronegativity which are linked together.

A third reason which appears to maintain the value of the discrepancy in the nitro-compounds at a higher figure than in many other molecules may lie in the unusually high density of these compounds. This feature is quite striking; for example, in para-dinitrobenzene it is 1·64, in meta-dinitrobenzene it is 1·57 and in 4-4' dinitrodiphenyl it is 1·45, while in most organic molecules containing only light atoms the density is about 1·1 to 1·2. The reason for the increase in density, of course, is the strongly

polar nitro-group, which forms multiple bonds of various kinds resulting in an unusually compact crystal arrangement.

The effect of this increased density is to diminish the average volume occupied by each atom in the unit cell, and when this results in the projection area for an atom to fall below a certain apparently critical value, some disturbance in the electron density contours appears to ensue. A rigorous analytical treatment has not been attempted here, for it would be necessary to show that the relation

$$\rho(x,y) = \frac{1}{A}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F(hk0)\, e^{-2\pi i\left(h\frac{x}{a} + k\frac{y}{b}\right)} \qquad (1)$$

does not accurately define the atomic centres when $\underline{a}$ and $\underline{b}$ become less than some certain value for each parameter. Some weight, however, may be lent to this suggestion that the high densities of these compounds has materially affected the discrepancies and hence the accuracy of the atomic co-ordinates, by the results of a simple one-dimensional experimental study of an hypothetical structure.

The 'molecule' C_6O_2 is set up in a triclinic cell of space group P_1, with $\alpha = \beta = \gamma = 90°$ and $a = b = 3{\cdot}5$Å., so that the third primitive transalation $\underline{c}$ may be varied inversely with the density. The only element of symmetry present is a centre, chosen as the origin, and since $\underline{a}$ and $\underline{b}$ are so small, the 'molecule' must lie entirely parallel with the $\underline{c}$-axis. The following co-ordinates were assigned; $C_1 = 0{\cdot}600$, $C_2 = 1{\cdot}800$, $C_3 = 3{\cdot}000$ and $O_1 = 4{\cdot}200$Å. (half the

'molecule' provided the asymmetric unit), and the lengths of c corresponding to the densities 1·10, 1·20, 1·30, 1·40 and 1·50 were found to be 12·7, 11·7, 10·8, 10·0 and 9·3Å. respectively. The structure factors for these five cells were then calculated, using the atomic scattering curve for benzoquinone (Robertson, 1935), for all the (001) planes reflecting up to $\sin\theta = 1{\cdot}000$. These F-values were then inserted in the expression

$$\rho(z) = \frac{1}{c} \sum_{-\infty}^{+\infty} F(001)\cos 2\pi l \frac{z}{c} \qquad \text{(2)}$$

from the evaluation of which the contours in Fig. 2. were obtained, the true atomic positions being indicated by the small lines.

It was found by a comparison of the apparent atomic centres, taken from these contours, with the true centres, that the following differences existed, the values given in Table I being averaged over all five atoms.

TABLE I

Variation of atomic centres from true positions with change in density.

density	1·10	1·20	1·30	1·40	1·50
difference	0·010	0·010	0·015	0·025	0·030 Å.

If errors of this nature are also found in two-dimensional Fourier syntheses, it is possible that apparent shifts of the order of 0·04Å. will occur, when the density is high.

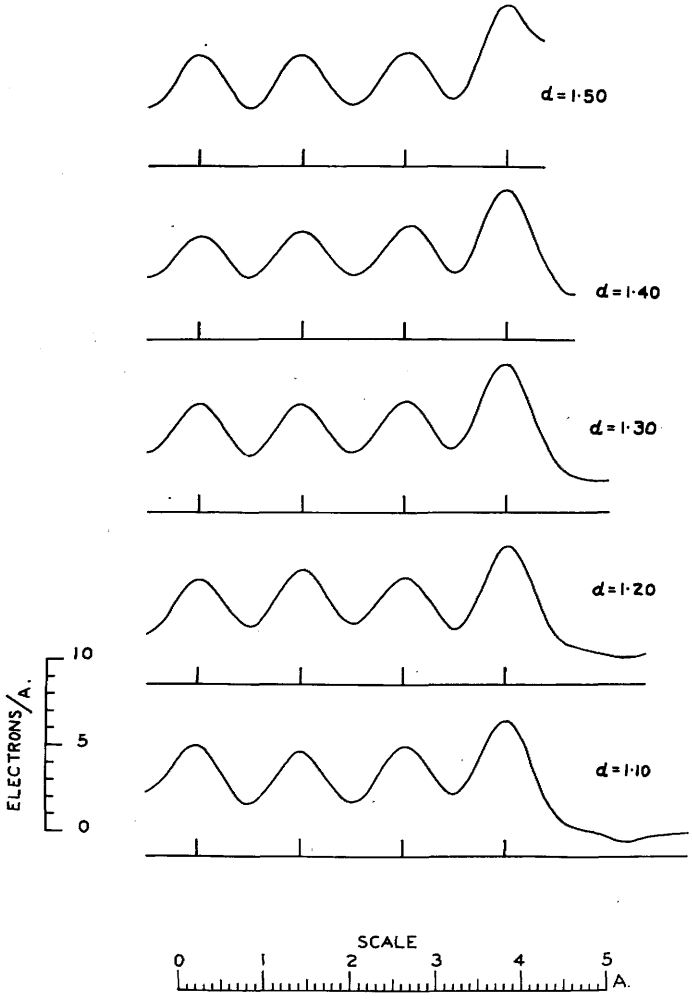


Fig. 2. One dimensional Fourier contour diagram showing the variation of contour from the true position with increase in density, the asymmetric unit only being illustrated.

This would hence go a long way towards accounting for the high discrepancies obtained in these compounds of high

density.

The preceding review thus shows that the accuracy of the work done up to this time is of somewhat variable quality, and in an endeavor to shed a little more light upon this field, the present study (Abrahams and Robertson, 1948) is one more contribution. The crystal structure of para-nitraniline is also of special importance in the study of inter-molecular attractions and in the formation of molecular compounds. It has long been known that aromatic nitro-compounds form coloured, stable and isolable complexes with aromatic polycyclic hydrocarbons, especially if the latter contain amino groupings. The precise mechanism of the attraction between these two components has been a matter of speculation for some considerable time, and it may readily be shown that para-nitraniline itself behaves physically as a self-molecular complex. Thus t he study of the crystal structure of this compound may also add to the existing knowledge of the nature of this organic molecular bond.

An almost entirely separate problem from those previously discussed is the nature of the variation of bond lengths in the aromatic ring. Measurement of bond lengths in polycyclic aromatic hydrocarbons by diffraction methods in recent years (Robertson and White, 1945; 1947b; 1947c; White, 1948) has shown quite conclusively that a considerable

variation is, in fact, observable. The experimental technique has been such that this variation may be regarded as real (Robertson and White, 1947a; Robertson, 1948a) and the range of bond lengths so observed has been between 1·37 and 1·45Å. Some calculations based on the simple assumption that if the percentage of double bond character in a particular linkage is known, then the bond length may be obtained from the empirical curve connecting bond lengths and bond character (Pauling and Brockway, 1937) have been carried out, and these largely agree with the observed variations.

In view of the considerable amount of research now published on this subject, it is obviously desirable that a fuller knowledge of the bond lengths in the simpler aromatic hydrocarbons be obtained. This would then permit of more elaborate wave-mechanical calculations and consequently, a more rigorous comparison of the theory with experiment. The molecules which most suitably lend themselves to this treatment are clearly, benzene itself, naphthalene and anthracene. The first of these would be difficult to study completely by x-ray diffraction methods, and so attention has been fixed on the other two compounds.

The early structural determinations of naphthalene and anthracene (Robertson, 1933a and b) were elucidated by means of the double Fourier synthesis method. Since these structures were taken very nearly to the limits of the method,

it is unlikely that any further refinement of the atomic co-ordinates could be obtained by the same means, with resulting increase in the accuracy of the bond lengths, due to the large amount of overlapping in the projections. This has the effect of placing a serious uncertainty in the co-ordinates of several of the atoms in the best projections.

The only way to overcome this difficulty is to carry out a full three-dimensional Fourier synthesis, so that each atom will be fully and separately resolved, enabling the atomic centres to be fixed with great accuracy. Such a synthesis would involve three main factors; a careful determination of the intensities of all possible reflecting planes, the accurate numerical evaluation of the triple Fourier series and finally, a precise transference from the electron density figures to the atomic co-ordinates. Both the first and the third of these factors principally involve experimental points of technique, and so need not be discussed at this stage. However, a fair range of computation methods are now available and a selection had to be made from them. These methods may be grouped into two main classes; those which are readily operated manually, and those which involve the use of some mechanical or electronic process.

The first of the manual methods was published in 1934 (Beevers and Lipson, 1934) in which the triple Fourier series

was reduced $\rho(x,y,z,) = \sum\left[\cos 2\pi \underline{x}.\sum\left\{\sin 2\pi k\underline{y}.\sum(\right.\right.$

$$\rho(x,y,z,) = \sum\left[\cos 2\pi \underline{x}_a.\sum\left\{\sin 2\pi k\underline{y}_b.\sum(F\sin 2\pi l\underline{z}_c)\right\}\right] \quad \text{---(3)}$$

and by tabulating the functions $\pm A\cos 2\pi h(\underline{n}/60)$; $\pm A\sin 2\pi h(\underline{n}/60)$, in which, for constant values of $\underline{h}$ (0,1.....20) each value of A, from 0 to 99 are given, the series may be completely summed by three sets of single summations.

The Beevers-Lipson method is very rapid, but suffers from the disadvantage that the value of the functions tabulated are only correct to two figures, so that the final electron density values obtained are not very reliable. This disadvantage is surmounted by the Robertson sorting board (Robertson, 1936 a and c) in which the functions $\begin{pmatrix}\sin\\ \cos\end{pmatrix} 2\pi h(\underline{n}/60)$ are tabulated, with the values of h=1 and n = 1,2.....15. Thus integral values of $\underline{nh}$ from 1 to 15 may be obtained. A separate set of strips with all amplitudes from 0 to 1000 was also constructed, and hence the functions $A\begin{pmatrix}\sin\\ \cos\end{pmatrix}2\pi h(\underline{n}/60)$ may readily be obtained. This method gives three accurate significant figures, which is very satisfactory for normal usage, but takes rather longer than the Beevers-Lipson strips.

A later technique (Patterson and Tunell,1942) is based on the Robertson method, but instead of requiring a large number of strips to be moved at each stage in the summation, a series of masks are placed over the strips, which carry the same value as on the sorting board. This

makes for somewhat greater speed, but has the disadvantage of placing a considerable strain upon the operator, since the positive and negative numbers are now denoted not by + or - signs, but by colours. The holes which select the positive values are left unmarked, while those corresponding to negative values are ringed in red. If the number on the strip below is also negative, so that a red number is seen through a red hole, this has to be taken as positive. However, the Patterson-Tunell strips are faster than the Robertson sorting board and just as accurate.

A very recent development is a new stencil method (Robertson, 1948b) in which the original accuracy of the boards has been retained, and the positive and negative values of each $A\begin{pmatrix}\sin\\\cos\end{pmatrix}2\pi h\,(\frac{n}{60})$ is seen as a + or - sign. The speed of operating this method is quite comparable with the Beevers-Lipson strips, being only about 10 - 15% longer, and the strain upon the operator is quite negligible. It seems likely that this method will largely replace the other older ones.

The various mechanical computing machines are described quite fully by Booth, 1948, in which he includes accounts of the several hand machines (Cox,1939; Booth, 1947; Evans and Peiser, 1942) but these machines only deal with one_dimensional summations, although it appears possible (Robertson, 1932) to extend such machines to multi-

dimensional summations.

A number of electro-mechanical devices (Maxwell, 1940; Beevers, 1939; Beevers and MacEwan, 1942; Rymer and Butler, 1944) have also been described by Booth in his recent book, but none of these has yet passed into general use. Some of the earlier electronic devices now appear to have given way (Somerville, 1944; Rivlin and Booth, 1944) to the more recent development of the oscillographic Fourier synthesiser (Pepinsky, 1946; 1947; 1948).

The operation of the synthesiser is based upon Bragg's early method for photographic summation of simulated interference fringes. The required sinusoidal light intensity variations are produced on the screen of a cathode ray tube by means of a television scan and intensity modulation of the cathode ray tube grid; the light pattern is then locked in position by complete synchronisation of the modulation and sweep signals, e.g., by using 1000 cycle sine waves. The amplitudes of the Fourier coefficients are supplied to the machine as settings of individual controls on a series of potentiometers, and the phases (0° and 180°) are entered by means of double-throw switches for each term. A complete centro-symmetric plane projection of the electron density, corresponding to a specific set of amplitudes and phase values will then appear on the screen, and the effects of changing the phase of one or any number of terms are immediately observable on the screen. Indices up to 20 for

each h_1, h_2..... term can be used. The cell size and angle are variable at will on the oscillographic screen, and a close examination of the picture may be obtained either by direct photography, or by the use of a photo-cell on the screen.

The most valuable machine at present available, however, for both fairly rapid and accurate three-dimensional summations, is the Hollerith International Business Machine. In this device, a punched card system is used in which the positions of the punched holes correspond to the magnitude and phase (positive or negative) of the Fourier term. The general method used by the International Business Machine is outlined by Booth in his book. Once a set of cards with all amplitudes from 0 to 1000 have been punched for both positive and negative terms, any particular summation will only require a set of master cards to set the machine in operation for the desired function. The most complicated part of the Hollerith machine is the wiring panel which controls the possible operations permitted. At least two types of wiring circuit are now in use, one in the United States, in Pauling's laboratory in the California Institute of Technology and in Evans' laboratory in the Massachusetts Institute of Technology, and the other in Britain, as used by Comrie in the Scientific Computing Service in London. It seems that the latter has the more effective circuit, for

it permits cross-checks of the printed figures to become automatic, whereas in the American circuit, checking is usually carried out by repeating an operation. The present author, however, is of the opinion that whilst the Hollerith system is very desirable in three-dimensional summations, for it enormously reduces the labour required, the time needed in selecting the appropriate cards for a two-dimensional summation is almost as great as in actually manually carrying out the summation with the Robertson stencils. The only advantage in using an International Business Machine in such cases would lie in its imposing less strain on the operator.

THE CRYSTAL STRUCTURE OF PARA-NITRANILINE

Crystal Data. para-Nitraniline, $NO_2.C_6H_4.NH_2$; molecular weight, 138·1; melting point, 147·5°C; calculated density, 1·422; measured density, 1·418; monoclinic prismatic, $a = 12·34 \pm 0·02$, $b = 6·02 \pm 0·02$, $c = 8·63 \pm 0·02$Å., $\beta = 91°40'$. Absent spectra, (h0l) when h+l is odd, (0k0) when k is odd. Space group C_{2h}^5 ($P2_1/n$). Four molecules per unit cell. No molecular symmetry required. Volume of the unit cell, 640·7Å.^{3} Absorption coefficient for x-rays, $\lambda = 1·54$Å., $\mu = 10·7$ per cm. Total number of electrons per unit cell = F(000) = 268.

Earlier determinations of the crystal data have been given by Groth, 1917, and by Prasad and Merchant, 1938. These authors used the space group $P2_1/c$ with the constants $a = 15·31$, $b = 6·08$, $c = 8·63$Å. and $\beta = 126°11'$. Remeasurement of the cell gave the values 15·23, 6·02, 8·63Å. and 126° 58' which compared fairly well with the earlier data. However, it was more convenient to change to $P2_1/n$ as above, to allow a better comparison to be made with para-dinitrobenzene (Abrahams and Robertson, 1947), where the measured parameters are $a = 11·07$, $b = 5·47$, $c = 5·67$Å and $\beta = 92°18'$. It is readily seen that the principal difference between the axial parameters of para-nitraniline and para-

dinitrobenzene lies in an increase in the length of the c-axis, and it was thought that some aid might be obtained in solving the trial structure of the former compound by analogy with the latter. As it eventually materialised, however, this apparent resemblence proved somewhat misleading.

The dipole moment of para-nitraniline has been measured (Kumber and Porter, 1934) in solution in dioxan, and found to be 6·68D., which value is rather anomalous, since aniline has a moment of 1·56D. and nitrobenzene a moment of 4·0D., so that para-nitraniline cannot consist of a simple undistorted nitro-group and amine-group in the para-position to each other in a simple undistorted benzene ring. Other more recent values confirm this figure, as being 6·17D. in benzene and 6·81D. in dioxan (Vassiliev and Sirkin, 1941).

The optical data available (Winchell,1943) is very scanty, for only two refractive indices have been measured at 1·78 and 1·556, and these values are not sufficiently different to give rise to any belief in a strong birefringence, which might have aided the trial structure.

Analysis of the structure. The unit cell contains four general positions, and as there are four molecules in the cell, it follows that each molecule is an asymmetric unit. The analysis of the structure thus becomes rather complicated, and this is made worse by the absence of many outstanding features in the intensity distributions among the various

spectra. It thus became necessary to employ trial and error methods, based on the known chemical structure and the standard covalent radii for the atoms involved.

There are several methods available for the solution of a trial structure. The most direct way is to insert a heavy atom into the structure, so that, on obtaining a set of experimental relative structure factors, these may at once be introduced into a Patterson summation (Patterson,1934). Such a series is of the form

$$P(x,y,z,) = \sum_{-\infty}^{+\infty}\sum_{h,k,l}^{+\infty}\sum_{-\infty}^{+\infty} |F(hkl)|^2 \cos 2\pi\left(\frac{hu}{a} + \frac{kv}{b} + \frac{lw}{c}\right) \quad (4)$$

and since only the squares of the structure factors are used, it is not necessary to determine the phase angles. This expression enables the deduction of the inter-atomic vectors, and since the only important vectors are from the heavy atom, it is possible to fix the co-ordinates of this atom quite accurately, for these effectively swamp all others. Equation (4) is almost invariably summed over two dimensions, when it reduces to the form

$$P(x,y,) = \sum_{-\infty}^{+\infty}\sum_{h,k}^{+\infty} |F(hk0)|^2 \cos 2\pi\left(\frac{hu}{a} + \frac{kv}{b}\right) \quad (5)$$

If the structure is more complex, it is often advisable to use a Patterson-Harker series which uses more data and hence is more powerful (Harker, 1936). This is essentially the same as (4), but by making use of some symmetry in the space group, the series is reduced to a number of two-dimensional summations, in which all the (hkl) planes are involved.

Once the co-ordinates of the heavy atom have been accurately fixed, the phases appropriate to this position may be calculated, and the relative structure factors, with these phases attached, may then be inserted into a normal Fourier summation. It is then very likely that this operation will reveal the presence of the other lighter atoms present, in which case the usual methods of refinement may be used. A conspicuously succesful example of such a technique has been recently afforded by calciferol (Crowfoot and Dunitz, 1948) in which analysis the iodine atom was sufficient to disclose the remainder of the molecule.

Where no heavy atom is present, there are several other useful ways of avoiding the drudgery of pure trial and error methods. One of these is the Huggins' mask technique (Huggins, 1941; 1944; 1945) which consists of superposing a number of impressions from film on which the density distribution is given by $\cos 2\pi(\frac{hx}{a} + \frac{ky}{b})$ and the exposure time is proportional to the magnitude of the co-efficient. This method enables fairly rapid changes in phase to be carried out and the consequent change in electron density to be observed, and is in effect, a qualitative modification of the Pepinsky oscillographic synthesiser (see page 19).

Another method is that of Harker and Kaspar (Harker and Kaspar, 1947; 1948; Gillis, 1948), who have demonstrated

that relations between the magnitudes of some F(hkl)'s and the signs or phases of others may be obtained by the application of Schwarz's and Cauchy's Inequalities. It is thus possible, in principle, to obtain the phases of some Fourier co-efficients directly from the diffraction data. For the successful application of these relations, however, it is necessary (a) that the intensities be expressed on the absolute scale, and (b) that the atoms in the structure be all of about the same atomic number, so that a common scattering curve may be used. In practice, it is found that a supplementary condition is that there be a wide range in the values of the 'unitary structure factors', where these are a measure of the contributions of the atoms in the crystal to any given plane. It may thus be seen that this method is largely complementary to those of Patterson and Patterson-Harker.

A notable example which has been solved by this method is crystalline decaborane, where sufficient phases were determined to lead to a successful Fourier projection.

When none of these methods seems to apply, pure trial and error has to be relied upon, backed where possible, by as much other relevant physical data as may be obtained. If the molecule possesses a centre of symmetry, or some other special symmetry element which is used crystallographically by the molecule, the number of trials needed to fix the

atomic co-ordinates is considerably reduced. Thus, in the case where a molecule possesses a centre of symmetry, e.g., between two atoms, this point must coincide with the crystallographic centre of symmetry, and so the molecule is at once restricted to a definite part of the unit cell. If, further, there is an outstandingly strong plane or set of planes, the molecule must be pivoted about this fulcrum in such a way as to meet these conditions. The trial structure is hence comparatively straight forward, for even if the model used is out by as much as 15° in atomic co-ordinates, it is probable that the first Fourier summation will move the molecule in the correct direction.

When there is no useful symmetry element in the molecule, so that the whole molecule becomes the asymmetric unit, it is necessary to rely purely upon the x-ray diffraction data, and any other physical evidence that appears to be of value. Thus, a marked birefringence, with relation to the crystal axes, might help in fixing the tilt of the molecule. In the most general case, where no other data seems sufficiently decisive, the only information which may be used is the relative strengths of the reflecting planes.

In para-nitraniline, the optical data (see page 23) was not very helpful, and so the x-ray data alone was used. At first, an apparent resemblence to para-dinitrobenzene

was employed, for both compounds belonged to the same space group P_{2_1}/n and had $\beta = 92^\circ$ approximately. Unfortunately for this analogy to be of much help, the outstanding plane for para-dinitrobenzene was $(10\bar{1})$ while for para-nitraniline it was (202), so that the molecules most probably lay along opposite diagonals. A rough total tilt for the molecule was derived from a consideration of the respective lengths of the b-axis in the two compounds, and the known tilt of the para-dinitrobenzene molecule to the (010) plane. In the latter compound, $b = 5{\cdot}42$Å. and where θ is the total tilt, $\theta = 48^\circ 6'$; hence, for para-nitraniline, where $b = 6{\cdot}02$ Å., θ should be about 53°. A large number of models having this value for the total tilt were then constructed and critically examined.

The strongest plane was (202) where F(202) = 119 and the maximum value = 149. Thus the molecule was considered to lie with the greatest concentration of atoms parallel to this plane. This view was confirmed by the pronounced cleavage along $(10\bar{1})$. The relative weakness of (101), further made it appear likely that the bulk of the molecule would be concentrated on the (404) plane. Other fairly important planes were $(50\bar{7})$, $(70\bar{5})$ and (800), and so, using various models having a total tilt of 53°, a large number of positions were tried, to secure a relative fit among these few planes. An added difficulty, of course, lay in the fact

that the molecule, being non-centrosymmetrical, could face either direction, which duplicated all the possible positions (see Fig. 3).

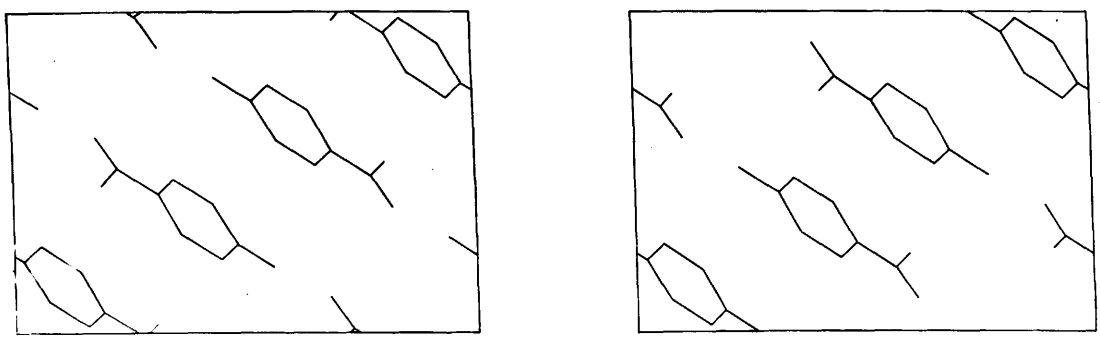


Fig. 3, Diagram showing possible alternative positions for the para-nitraniline molecules.

After exhaustive attempts along these lines had failed, the analogy with para-dinitrobenzene which had been the basis of these trial models, was considered to be entirely misleading. The possibility that the total tilt might be considerably more than 53° was then explored. In order to retain a small value for (101), once the total tilt is

increased past a certain amount, it has to become quite large. Now, the total tilt, θ, may be resolved into two component tilts mutually at right angles. The tilt parallel with the (101) plane may be named α, and the tilt normal to this γ, all being in a plane parallel with (010). These component tilts, α and γ, may be related to θ by the relation

$$\cos\alpha\cos\beta = \cos\theta$$

where

$$\tan\gamma = \cos\alpha\tan\beta.$$

i.e. β has the physical meaning that θ is obtained by first tilting the molecule through α, and then revolving it while in this tilted position, through β.

Thus, on increasing θ from the previous value to about 64°, α and γ could be varied at will. Examination showed that such variation could produce a model giving quite a reasonable agreement among the planes already considered, and so attention was widened to include other moderately important planes such as (004), (501), $(50\bar{1})$, $(10\bar{1})$, $(30\bar{1})$, $(60\bar{2})$, $(70\bar{1})$ and $(90\bar{3})$ and also the very weak planes of wide spacing (103) and (400).

After several adjustments had been made to this model, a set of atomic co-ordinates were found which gave some measure of agreement between the calculated and observed structure factors for these selected planes. This enabled the relative observed structure factors to be placed on the

same scale as the calculated structure factors, whereupon the structure factors for all possible planes were then calculated. The agreement was not very good, but further small shifts in the molecular model were found to improve the discrepancy. A most encouraging feature, during this tedious stage, was that on improving some specific planes, the general agreement became better, as well.

The structure factors for all the possible 134 (h0l) planes were eventually made to agree with the observed values so that Δ became 33%. Using the phases from this model, a first Fourier summation was evaluated, employing 62 terms. The atomic co-ordinates from this operation then gave a discrepancy of 25%, and extending the experimental range of intensities so that 110 (h0l) planes were observed, and recalculating the discrepancy, Δ was found to rise to 31%. A second Fourier summation brought this figure down to 26·5% and the next to 22·1%. A fourth summation had Δ equal to 18·5% and the fifth Fourier synthesis had the discrepancy down to 15·2%. At this stage, no further changes in sign were observed, and hence the refinement in the structure was regarded as being complete. Fig. 4. shows one molecule in projection on the (010) plane, and the estimated centres are indicated by small crosses. The explanatory drawing (upper part) is inverted by the operation of the centre of symmetry.

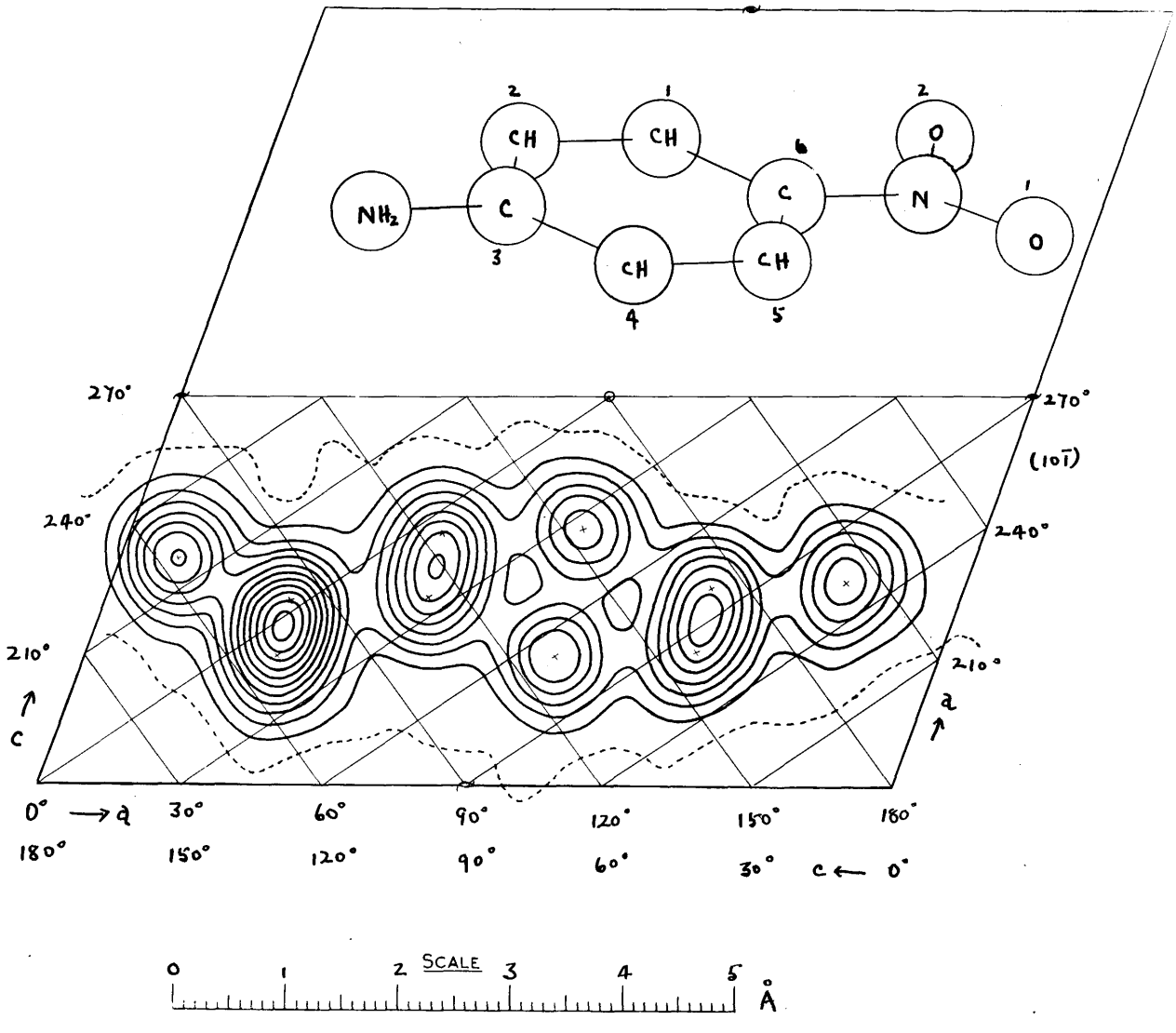


Fig. 4. Projection of the para-nitraniline molecule along the b-crystal axis on the (010) plane. The boundaries are the ac cell diagonals. Each contour line represents a density increment of one electron per $Å^2$, the one electron line being dotted.

The amino nitrogen atom, two of the carbon atoms, and one oxygen atom are well resolved in this projection, and the centres can be accurately marked. The estimated centres of the other atoms are consistent with the projection of a planar molecule containing a regular hexagonal benzene ring and a symmetrical nitro-group.

A smaller scale drawing is given in Fig. 5., which illustrates the relations of a group of nine molecules in the crystal structure. Hydrogen bonding between the amino- and nitro-groups at the ends of consecutive molecules is clearly one factor which stabilizes the structure, but in addition there appear to be strong lateral attractions between the rows of molecules. This has the effect of binding the rows together in pairs, with a larger gap between the next pair. The intermolecular distances involved in these relations are listed in Table V.

Although satisfactory definition has been achieved in the (h0l) projection, and reliable values for the x and z co-ordinates can be obtained from it, the evaluation of the third co-ordinate of the atoms is a matter of considerable difficulty. Even if a regular planar structure is assumed, there is still a free transalation for the molecule as a whole, along the b-axis, which must be determined from the intensities of the other zones of reflection.

It is possible to calculate the approximate tilts of

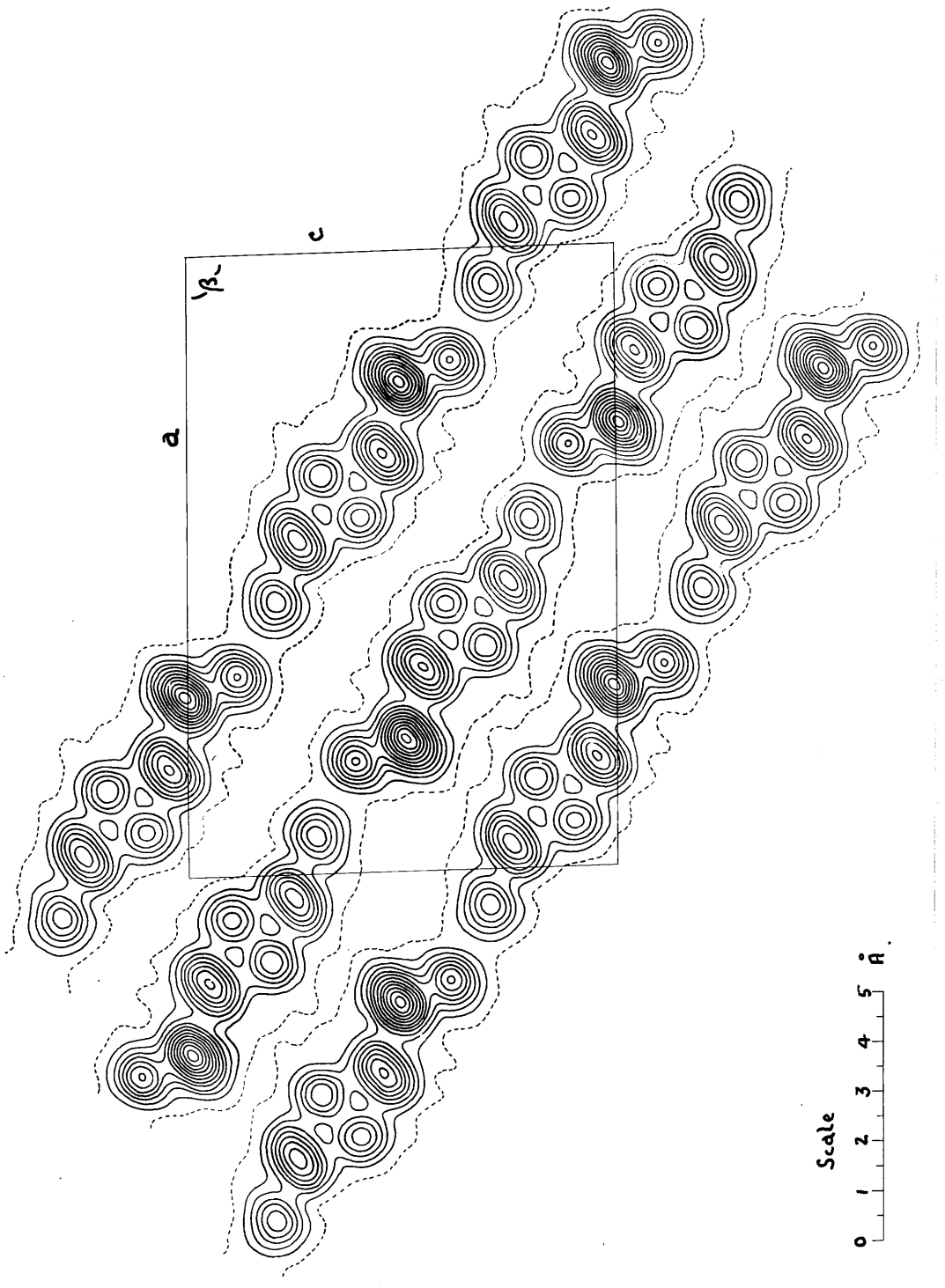


Fig. 5. The relations of a group of nine molecules of para-nitraniline in the b-axis projection. Contour scale as in Fig. 4.

the molecule in the (hk0) projection from the known x and z co-ordinates. These tilts were found to be compounded of $\alpha = 30^\circ$ and $\gamma = 50^\circ$ (using the same conventions as on page 30, but the tilts parallel with (001) instead of (010)), while the angle made by $C_6 C_3$ with the a-axis was calculated to be about 28°. Although at first sight, there may appear to be two possible positions which will satisfy these conditions, so that the angle of 28° may be either positive or negative, in fact they are identical, the only difference being in the position of the origin. In order to facilitate the determination of the free parameter parallel to the b-axis, a graphical method was adopted. In this, an arbitrary position on the b-axis was taken as the origin, and the values of the structure factors of three principal planes was calculated at 10° intervals, and plotted against the length of the b-axis. By virtue of the space group symmetry, the position at 180° from the origin is identical with that at the origin. The resulting graph is shown in Fig. 6.

It is clear from this figure, that in order to keep (110) large, and (020) and (040) of moderate and equal strength (the relative observed structure factors were placed on the (h01) scale by means of the common (001) planes), only two general positions are possible, at about 10° and 100°. The latter position is ruled out since (410) becomes

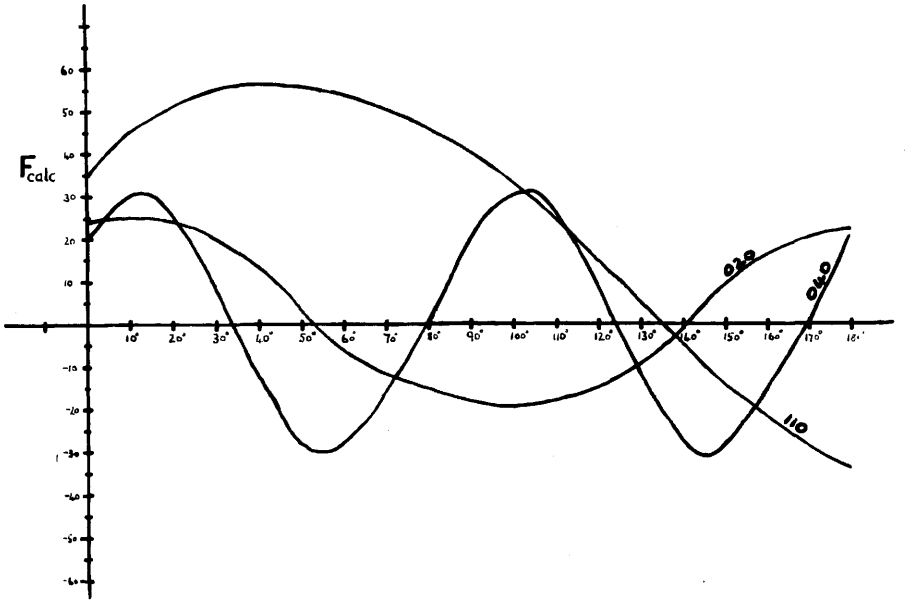


Fig. 6. Graph for the determination of the free y-parameter.

quite small there, and hence the region about 10° away from the origin marked will contain the correct position for the molecule. After sundry small adjustments to the tilts had been made to secure better agreement between the observed and calculated structure factors, a position about 5° from this origin was adopted, and a Fourier summation completed. The resulting contour map, although not defining the atomic positions sharply, seemed to warrant a second Fourier. On completing this, and recalculating the structure factors,

it was observed that the discrepancy was substantially unaltered, and also that no significant sign changes had occurred. This was taken to signify that the trial structure was wrong.

Further detailed examination of the observed spectra then led to the belief that the model would give a more reasonable fit at about the position 15°, on Fig. 6., and this general position, with the addition of various small adjustments gave a final position about 15° away from the first one tried, that seemed to have a fair agreement with the observed data. A Fourier summation on the basis of this molecular position, on completion, was found to have a discrepancy of 35·5% and quite good resolution was obtained. This figure, together with a number of changes in sign, indicated that the correct trial structure was now being used. It was of considerable interest to note that in this case, the Fourier method would not swing the molecule through the necessary 15°, a distance which was not very large since the b-axis was fairly small.

The apparent cause of this failure was that none of the geometrical structure factors were large, the maximum being 0·42 for (800). Even the plane of strongest intensity (110) had a value of only 0·28, and the general small value of the structure factors in the (hk0) zone had the effect of preventing the Fourier series from converging sufficiently

rapidly. Another related effect was in preventing the electron density contours from sharply defining the structure. These values for the geometrical structure factors may be compared with those in the (h0l) zone, where (202) has the value of 0·74. In all these cases, the maximum value for the geometrical structure factor is taken as unity.

The effect of shifting the molecule through 15° was to change the sign of 22 of the observed structure factors. There are only 63 observed planes altogether (96 being possible), so that this relatively small shift altered about 30% of the phases. The reason for this again lies in the small values of the geometrical structure factors, for when these lie between zero and 0·05, and no less than 30 planes in this zone fell into this category, sign changes are clearly quite easily made.

The phases obtained from this last Fourier summation were then used in a new synthesis, when the discrepancy became 31·5% and a third Fourier summation reduced this to 27%. A fourth summation produced a disagreement of 24%, and one more had a value of 23·5%. The final Fourier series was found to have a discrepancy of 22·1%, at which stage no further changes in sign were observed. The final results, with the explanatory diagrams, are given in Figs. 7. and 8.

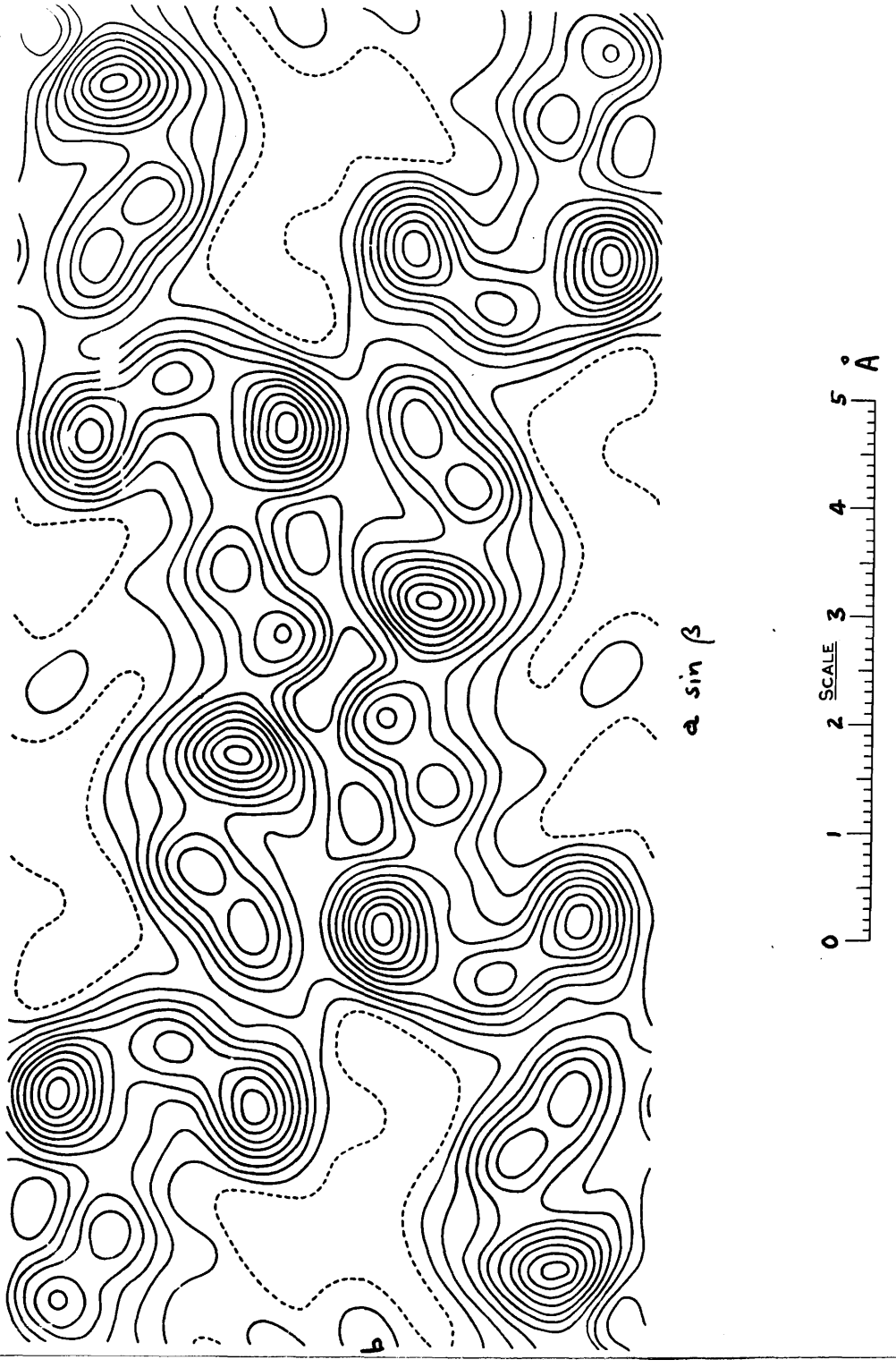


Fig. 7. Normal projection of the unit cell along the c-crystal axis. Contour scale; one electron per $Å^2$, the one electron line being dotted.

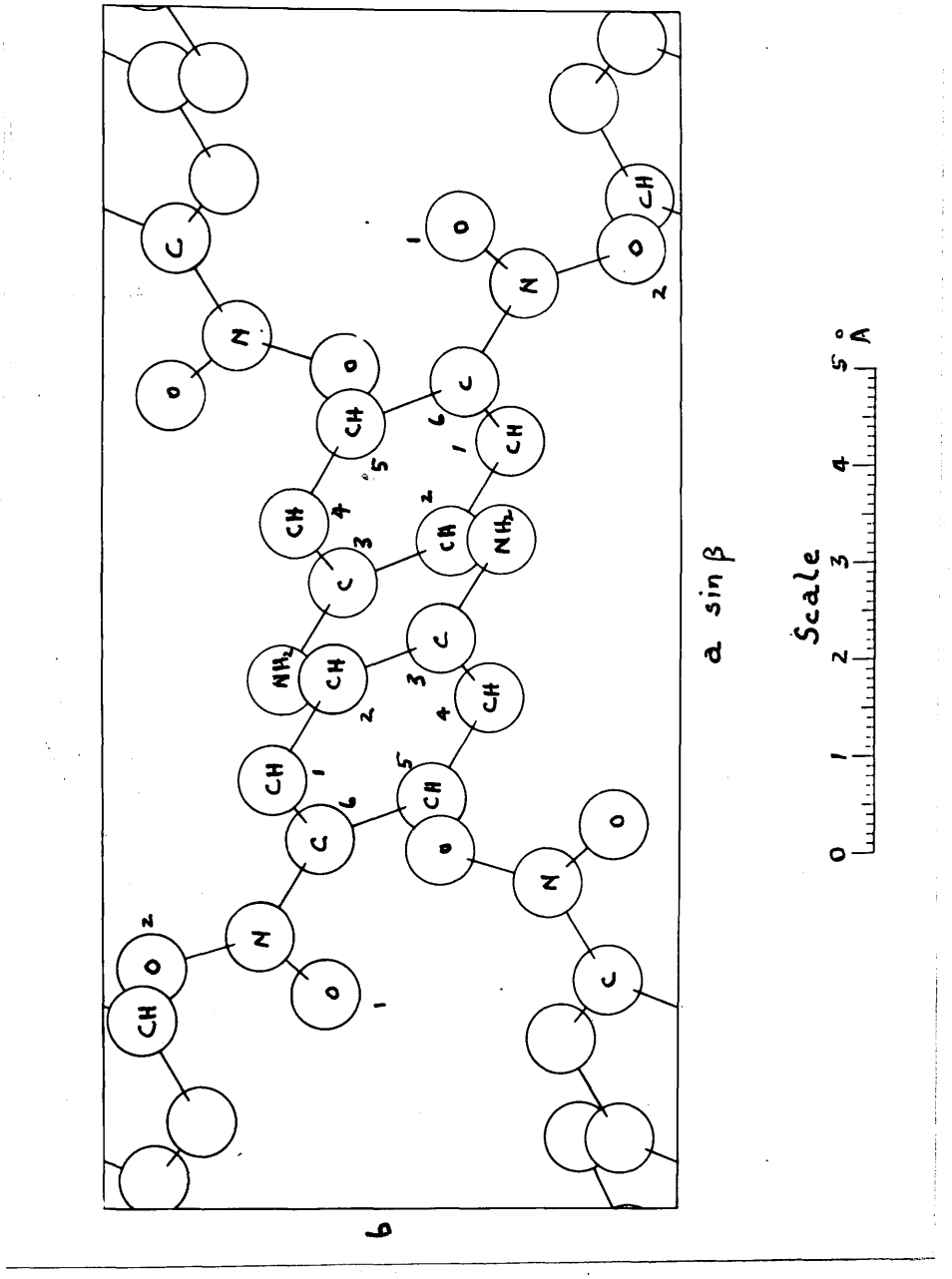


Fig. 8. Arrangement of the molecules in the c-axis projection.

Whilst this series of Fourier projections on the (hk0) zone was in progress, a parallel set of projections on the (0kl) zone were carried out, for these two zones were largely complementary. In particular, the (0kl) zone resolves O_2, which atom is not separately resolved in any other projection, and so reliable values for its y and z co-ordinates could be obtained. The progress made in this zone is shown by the following discrepancies, found after each successive Fourier summation; 35%, 33·5%, 32%, 26·2% and the final figure refers to the Fourier summation at the point where changes in sign had ceased. The results of the final projection are given in Figs. 9. and 10.

The three zonal projections thus allow direct measurement of the x, y and z co-ordinates of C_1, C_3, C_4, C_6, N_2 and O_1, and also the y and z co-ordinates of O_2. The positions finally assigned to the centres of the other atoms in these projections are those which appear to be most consistent with all the data.

One method of assessing the reliability of the results is by considering the discrepancy (see page 8). In the present investigation, the final discrepancies in the zones examined are found to be 15·2% for the (h0l) structure factors, 22·1% for the (hk0) structure factors and 26·2% for the (0kl) structure factors, with an average value of 19·4% for all these structure factors taken together. These

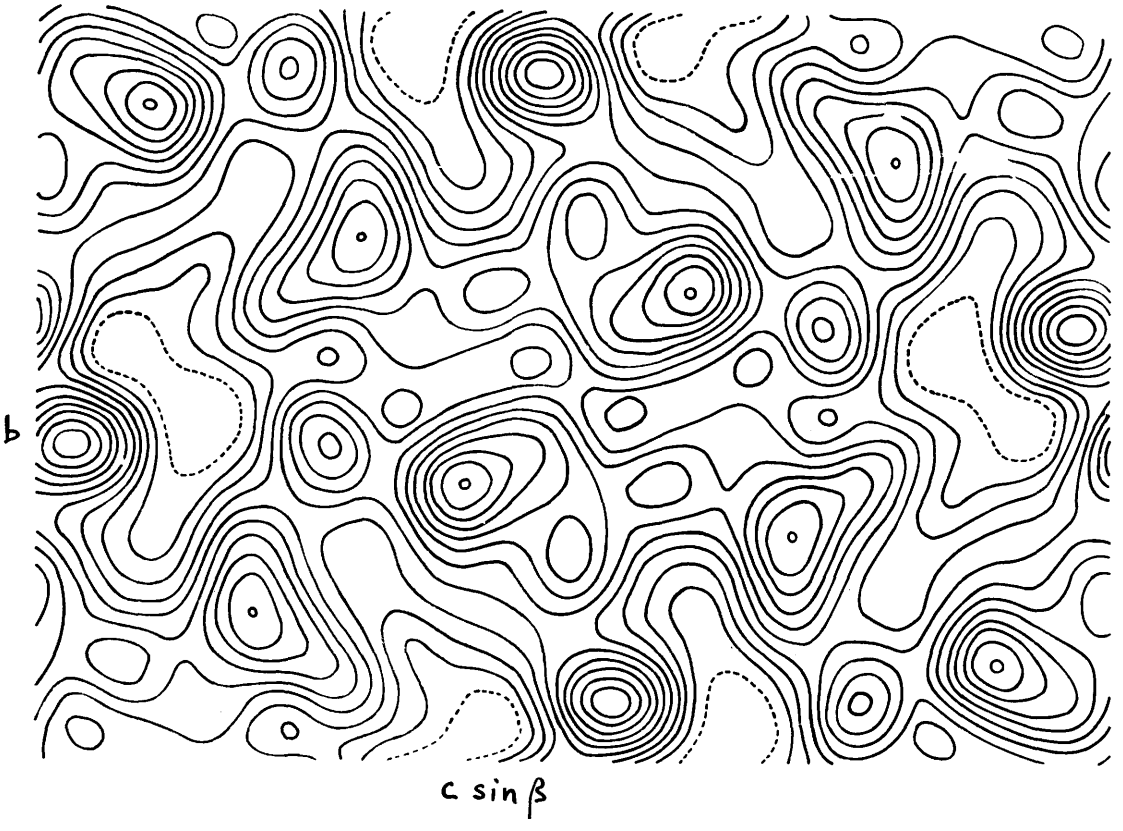


Fig. 9. Normal projection of the unit cell along the a-crystal axis. Contour scale; one electron per $Å^2$, the one electron line being dotted.

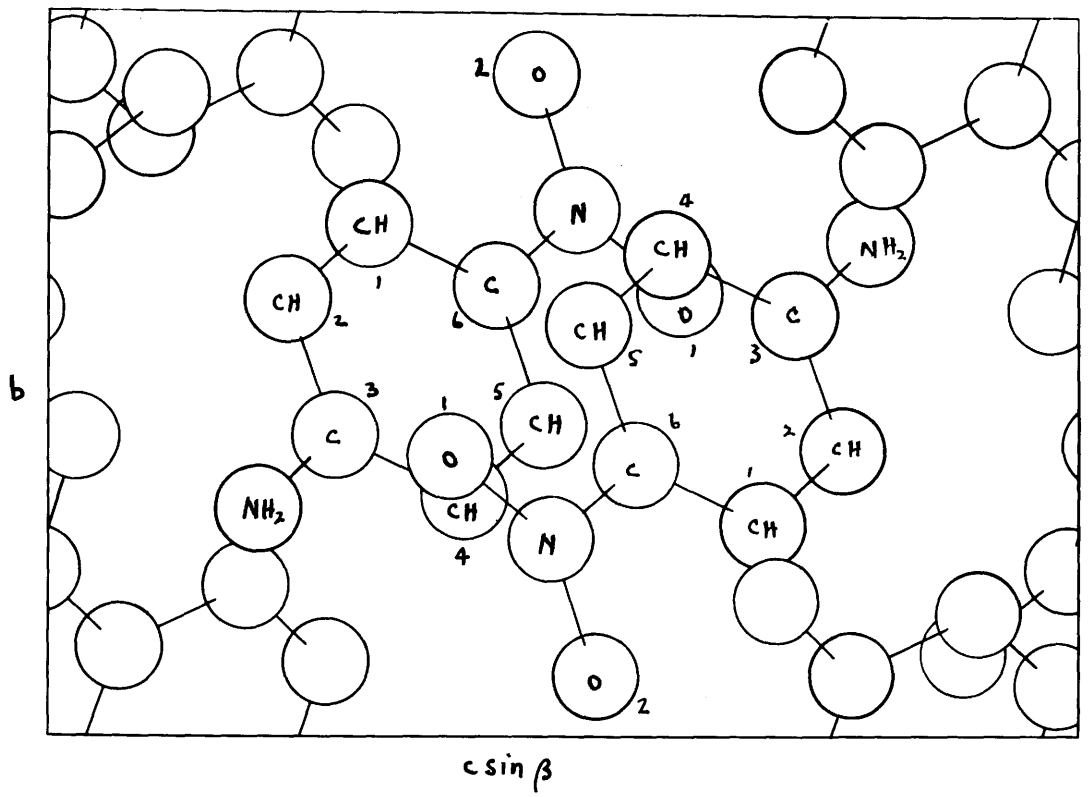


Fig. 10. Arrangement of the molecules in the a-axis projection.

figures are not unduly satisfactory, although they are considerably better than those obtained in other recent determinations of similar nitro-compounds (Archer, 1946; Gregory and Lasettre, 1947; Llewellyn, 1947).

The comparatively large values of the discrepancy in the (hk0) and (0kl) zones mentioned above are probably due more to the small average value of the observed structure factors in these zones than to serious errors in the atomic co-ordinates. This may be demonstrated by expressing the discrepancies in the form $\frac{\Sigma|F_{obs.} - F_{calc.}|}{\Sigma|F_{max.}|}$, where Fmax. represents the maximum value that the structure factor would have if all the atoms made contributions in phase to that particular plane, i.e. if all the atoms lay exactly on that plane. On this basis, the discrepancies become 2·68%, 3·05% and 3·25% for the (h0l), (hk0) and (0kl) zones respectively. If these figures are placed on the original scale for the (h0l) zone, they become 15·2%, 17·2% and 18·4%, showing that the results obtained for all three zones are reasonably comparable. This method of assessing the discrepancy in a structure might quite well be extended, for it would then make comparisons much less dependent upon chance distributions in the values of the geometrical structure factors.

Co-ordinates and Dimensions. The *x* and *z* co-ordinates obtained from Fig. 4. are probably the most reliable. The *y* co-ordinates of all the atoms except N(1), C(5) and C(2)

may be obtained directly from Figs.7. and 9. The other y co-ordinates are deduced by assuming that the figures are projections of regular planar hexagons and that N(1), C(3), C(6) and N(2) lie on a straight line, assumptions that are justified by the b-axis projection (Fig.4.). The results are given in Table II, where the co-ordinates are expressed in Ångstrom units and also as fractions of the axial lengths in degrees. The co-ordinates referred to the monoclinic crystal axes are denoted by (x, y, z,) while the co-ordinates referred to orthogonal axes are denoted by (x', y, z',), where the orthogonal axes are a', b and c, and a' is an axis chosen perpendicular to the b- and c-crystal axes. These orthogonal co-ordinates are useful for calculating interatomic distances, and are derived from the monoclinic crystal co-ordinates by the relations

$$x' = x + z\cos\beta$$

$$z' = z\sin\beta$$

As β is $91°40'$ in this crystal, z and z' are equal to within the limits of measurement.

TABLE II

Co-ordinates referred to crystal axes.
Origin at the centre of symmetry.

Atom cf. Fig.4.	xÅ	x'Å.	$2\pi\frac{x}{a}$	yÅ.	$2\pi\frac{y}{b}$	z=z'Å.	$2\pi\frac{z}{c}$
NH_2	6·90	6·85	201·4°	1·87	111·8°	1·74	72·8°
CH(1)	4·42	4·34	128·8	4·25	254·1	2·66	111·1
CH(2)	5·46	5·40	159·3	3·66	216·7	1·98	82·8
C(3)	5·90	5·83	172·1	2·50	149·4	2·39	99·5
CH(4)	5·28	5·18	154·2	1·99	119·0	3·46	144·3
CH(5)	4·25	4·13	124·1	2·59	154·9	4·13	172·2
C(6)	3·82	3·71	111·4	3·75	224·5	3·73	155·6
N	2·80	2·68	81·8	4·38	261·8	4·41	184·0
O(1)	2·21	2·06	64·6	5·69	220·9	5·28	220·2
O(2)	2·42	2·30	70·6	5·53	329·5	4·06	169·5

The atomic centres given by these co-ordinates are co-planar to within narrow limits (less than 0·04Å.) and they satisfy the equation

$$x' + 0{\cdot}74y + 1{\cdot}30z' - 10{\cdot}30 = 0$$

The carbon-carbon distances within the benzene ring are found to vary fron 1·31 to 1·39Å., the shorter distances being CH(2)-C(3), CH(5)-C(6), C(3)-CH(4) and C(6)-CH(1). The two remaining distances, CH(1)-CH(2) and CH(4)-CH(5)

give the normal bond length of 1·39Å. These divergences from the standard distance of 1·39Å. for the aromatic linkage were rather surprising, and in order to test them to ascertain whether they had any real physical significance, the y co-ordinates of CH(1), CH(2), CH(4) and CH(5) were modified so as to make the aromatic ring truly hexagonal. These modified co-ordinates are listed in Table III.

TABLE III

y co-ordinates required for a regular hexagonal benzene ring.

Atom	yÅ.
CH(1)	4·39
CH(2)	3·76
CH(4)	1·89
CH(5)	2·49

The discrepancies obtained in the (hk0) and (0kl) zones of structure factors with these new co-ordinates were found to be 28·7% and 35·5%, or when calculated on the basis of Σ Fmax., to be 22·5% and 26·8% respectively (compare pages 41 and 44). These figures show that the variations in bond lengths are almost certainly genuine, although the relatively poor definition of the projections which define the y co-ordinates makes it difficult to place great reliance upon the actual values obtained. It may also be significant that the one well resolved projection (Fig. 3.) gives a

benzene ring which could be the projection of a regular planar hexagon.

The other interatomic distances within the molecule, and the valency angles are listed in Table IV.

TABLE IV

Interatomic distances and valency angles.

N - O(1)	= 1·26Å.	O(1) - N - C(6)	= 117°
N - O(2)	= 1·26	O(2) - N - C(6)	= 120
O(1)···O(2)	= 2·22	O(2) -N - O(1)	= 123
C(4) - N	= 1·39	C - C distances in the ring	= 1·31 - 1·39Å.
C(3) - NH_2	= 1·36		

The nitro-group is seen to be symmetrical, and it lies in the plane of the benzene ring. The oxygen-nitrogen-oxygen valency angle appears to be slightly greater than 120°, probably due to mutual repulsion between the oxygen atoms. The bond lengths are probably accurate to within ±0·03Å. and the angles to within ±3°, but the precise limits are difficult to estimate.

Intermolecular Distances. The approach distances between atoms of adjoining molecules in the crystal structure may be calculated when the atomic co-ordinates (Table II) are combined with the co-ordinates of the equivalent points for this space group. These are given by the following

relations;

(A) x, y, z (B) $\frac{a}{2} - x, \frac{b}{2} + y, \frac{c}{2} - z$

(C) $\bar{x}, \bar{y}, \bar{z}$ (D) $\frac{a}{2} + x, \frac{b}{2} - y, \frac{c}{2} + z.$

In any structural determination of this nature, the interesting distances are those which fall below 4Å. and especially those which are less than the normal van der Waals approach distance of about 3·5Å. These values are collected in Table V, and the dispositions of the stronger intermolecular attractions are indicated by the dotted lines in Fig. 11. The closest approach distances occur between the oxygen atom O(2) and the carbon atoms of one of the adjoining benzene rings. Three of these distances are between 2·7 and 3·0Å., values which indicate rather powerful bonding forces between the molecules. A very interesting feature is that the join of O(2)A and CH(2)B, where the approach distance is smallest, is normal to the plane of the benzene ring, at the point CH(2)B. It should be noted that the centres of the molecules marked A and B are separated by half a transalation along the b-axis (which is normal to the plane of the diagram) by the operation of the two-fold screw axis. Thus the intermolecular bonds between these molecules, indicated by the dotted lines, do not really form a closed circuit as might appear from this diagram, but return to another molecule A', one transalation further along the b-axis and situated vertically above the one drawn.

The molecules are therefore not linked in pairs by these bonds, but form a helical arrangement, which links pairs of sheets of molecules, extending right through the crystal. This kind of arrangement has been observed in other crystals, notably in the hydrogen bonding of the resorcinol structure (Robertson, 1936d).

TABLE V

Intermolecular Distances

Oxygen-Nitrogen	O(1)A....NH_2(D)	3·07Å.
	O(2)A....NH_2(D)	3·11
Oxygen-Carbon	O(2)A....CH(1)B	3·03
	O(2)A....CH(2)B	2·66
	O(2)A....C(3)B	2·99
	O(2)A....CH(4)B	3·55
	O(2)A....CH(5)B	3·89
	O(2)A....C(6)B	3·69
Nitrogen-Carbon	N(A).....CH(2)B	3·70
	N(A).....C(3)B	3·68
Carbon-Carbon	C(3)A....CH(5)C	3·38
	C(3)A....C(6)C	3·60
	CH(4)A...CH(1)C	3·60
	CH(4)A...CH(4)C	3·38
	CH(4)A...C(3)C	3·38
	CH(4)A...CH(5)C	3·39
	CH(4)A...C(6)C	3·49
	CH(4)A...CH(2)C	3·55
	CH(5)A...CH(2)C	3·60
	CH(5)A...CH(1)C	3·69
	CH(5)A...C(3)C	3·37
	CH(5)A...CH(4)C	3·42
	C(6)A....CH(1)C	3·81
	C(6)A....CH(4)C	3·54
	CH(1)A...CH(4)B	3·96
	CH(1)A...CH(5)B	3·70
	CH(1)A...C(6)B	3·82

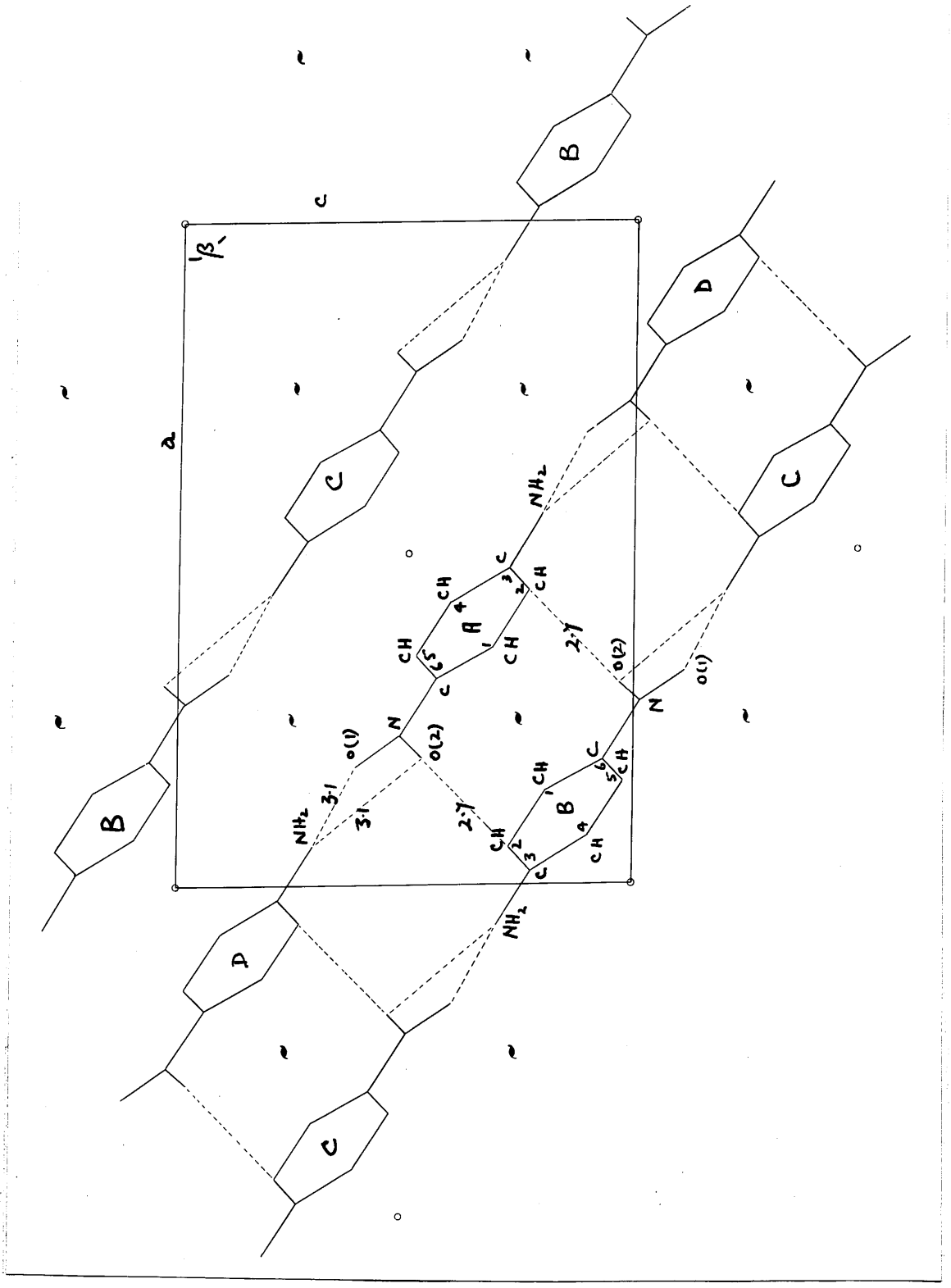


Fig. 11. Intermolecular approach distances. The structure is viewed along the b-axis, and the drawing is comparable with Fig. 5.

The end to end linking of the molecules is maintained by two moderately weak hydrogen bridges (3·1Å.) which extend from the amino nitrogen to the oxygen atom of the nitro-group of the next molecule. The helical arrangement referred to in the preceding paragraph also applies to these hydrogen bridges, the two bridges from any one amino nitrogen atom being directed towards the oxygen atoms of nitro-groups at different levels, along the b-axis, although in the projection as drawn in Fig. 11. they appear to form a closed circuit.

The carbon-carbon approach distances between the molecules A and C (Table V, Fig. 11.) are all of the usual van der Waals type and range from the graphite value of 3·4Å. to about 3·8Å. The carbon-carbon approaches in the case of the more closely linked molecules A and B, are all greater than 3·7Å.

Discussion. It is necessary to discuss the finer points of this structure with some caution, because the poor resolution of certain atoms makes the error limits in the determination of the bond lengths rather uncertain. The results (Table II) are in favour of a symmetrical nitro-group, lying in the plane of the benzene ring, and this agrees with several of the more recent determinations of the structures of other aromatic nitro-compounds (see introduction). The nitrogen-oxygen distances, at 1·26Å. are

slightly greater than the values of 1·20 and 1·23Å. found in meta- and para-dinitrobenzene respectively. On the other hand, the carbon-nitrogen distances of 1·36 - 1·39Å. are distinctly less than might be expected for the type of groupings involved in this molecule, and are similar to those found in fully conjugated carbon-nitrogen systems, such as the inner ring of the phthalocyanines (Robertson, 1936b). The precise value of this bond, as also the exact nature of the distortions from the standard 1·39Å. carbon-carbon distance in the benzene ring, may have to await a more exact three-dimensional determination. Nevertheless, it seems quite reasonable that the introduction of two such strongly polar groups as the nitro- and amine-groupings will have a considerable effect upon the electron distribution within the aromatic ring. Even the relatively non-polar aromatic ring itself, when fused to a second ring, causes considerable distortions, from 1·36 to 1·42Å., in the benzene nucleus (see section on naphthalene, Table IX).

The shorter bonds in the ring adjacent to the amino group may be accounted for by the fact that a larger concentration of electron material than normal will be found in the region around the ortho-carbon atoms, due to the directive influence of both substituents. Also, although the two other shorter carbon-carbon distances are not so readily explained, they may well be caused by a recession

of electrons from the oxygen to the nitrogen atom in the nitro-group, due to an induced form of dipole, and these electrons will tend to enter the two carbon-carbon bonds adjacent to the nitrogen atom, thus resulting in a shortening of these two linkages. Some evidence for this view may be obtained from a consideration of the lengths of the nitrogen-oxygen bonds in the nitro-group, which are rather longer than usual, indicating a flow of electrons away from them.

The most important aspects of this structure, however, lie in the intermolecular approach distances (Table V), and here the general conclusions still hold, even if some atomic positions should be uncertain by as much as 0·1Å. The hydrogen bonding between the amino groups and the nitro-groups at the ends of the molecules is relatively weak, at 3·07 and 3·11Å., but these distances are of the order to be expected in such a structure, and they correspond closely, for example, with the approach distances of 3·03Å. observed in urea (Wyckoff, 1932). This distance is greater than the average O - H···O approach of about 2·66Å., and this may be accounted for on the basis of the difference in electro-negativity between oxygen and nitrogen. Using the data given in the tables compiled by Pauling, 1942, the smaller value for nitrogen would increase the distance to about 2·98Å., assuming the hydrogen bond to be largely

proportional to the electro-negativity of the components. The listed values are stated to have an accuracy of ± 5%, and this uncertainty will be passed on to the calculated length of the hydrogen bridge.

The dominant feature of the present structure lies in the remarkably close approach distance of 2·66Å. which exists between one of the oxygen atoms of one molecule and an aromatic carbon atom of the next molecule. In all, there are three approach distances in the range 2·66 to 3·03Å., between this oxygen atom and the adjoining aromatic carbon atoms (Table V). All of these distances are far below the normal van der Waals approach of 3·4Å., and indicate powerful attractions of a new type. It seems very likely that this type of attraction may be the cause of some of the well known molecular complexes which are formed between aromatic nitro-compounds and polycyclic aromatic hydrocarbons. Several such complexes have been examined by the x-ray method (Powell, Huse and Cooke, 1943), but no definite evidence of such a close approach between the component molecules has yet been obtained. The complexity of the structures investigated, however, may account for the lack of a positive result.

The problem of the structure of the polynitro molecular complexes by chemical means has been particularly difficult, owing to the fact that their relative instability

has hitherto made it impossible to distinguish any chemical properties peculiar to the complexes themselves. A general review of the data shows that, if they are formed by mutual co-ordination of some kind between the components, the hydrocarbon or base is the donor molecule, and the nitro-compound the acceptor (Bennett and Willis, 1928). In general, the depth of colour of these complexes is roughly parallel with their stability, and the influence of polar groups substituted in either component is consistent with this view. Thus, their stability is often increased if an amino group is substituted in the hydrocarbon. Bennett and Willis also suggested that the molecular linkage must be directly to a carbon atom in the aromatic molecule, and not through a nuclear hydrogen atom, since hexa-methyl benzene forms a well defined complex with sym-trinitrobenzene.

This view is supported by the present study, which also shows that the intermolecular attachment is between the oxygen atom, and not the nitrogen atom, of the nitro-group and the aromatic carbon atom, as was proposed by Bennett and Willis. Briegleb, 1937, had suggested that the complexes were the products of electrical interactions between the polar nitro-compounds and electric dipoles induced, or already present in the aromatic hydrocarbon. This suggestion was repeated later on (Gibson and Loeffler, 1940), when it was believed that the molecular complex formation could

be regarded as an incipient oxidation - reduction process. Thus, when an aromatic group approaches a nitro-group, it is supposed that the induced dipole effect results in a projection of electrons from the aromatic group (oxidation) towards the nitro-group, in which a recession of electrons occurs (reduction) from the oxygen atom towards the nitrogen atom.

The present author believes that the key to this problem lies in the fact that the join of O(2)A and CH(2)B where the approach distance is smallest, is normal to the plane of the benzene ring. This would seem to indicate that the link is formed by the π-electrons of the aromatic carbon atom. The quantitative resonance treatment of the aromatic carbon atom considers the four available valency orbitals, described as s, p_x, p_y, and p_z, and combines the first three of these so that the three bond orbitals which are produced are coplanar and make 120° angles with each other. The fourth orb ital is that of p_z, which sweeps out lobes above and below the plane of the ring, and at right angles to the ring. The wave-mechanical treatment arrives at the same conclusion, in essence, that in an aromatic nucleus free π-electrons may be considered available at each member carbon atom, which are directed in a position normal to the aromatic ring.

It is well known from their chemical behaviour, that

the oxygen atoms in the nitro-group are strongly electrophilic. Thus, the situation may be considered in which an aromatic hydrocarbon possessing available π-electrons, in the form of an electron cloud held in a direction normal to the plane of the benzene ring, comes into contact with an oxygen atom in a nitro-group, which has a strong tendency to acquire electrons. In para-nitraniline, the nucleophilic tendencies of the π-electrons in the ortho-positions, with respect to the amino group, will be strongly enhanced by the directive influence of both substituents. Thus, the chance of forming a link with such an electron between the carbon atom to which it is attached, and some suitably oriented oxygen atom, is made quite likely.

In the present structure, it seems clear that para-nitraniline behaves as a self-complex, the nitro-group of one molecule acting as the 'acceptor', and a carbon atom ortho to the amino group in a separate molecule acting as the 'donor'.

A similar view is held by Weiss (1942; 1943; 1944), who, by a consideration of the dipole moments and the diamagnetic susceptibilities of a large number of molecular complexes of the type:

polycyclic aromatic hydrocarbon - polynitro compound

formed the opinion that the most likely type of bond would be of a partial ionic character. Complex formation would

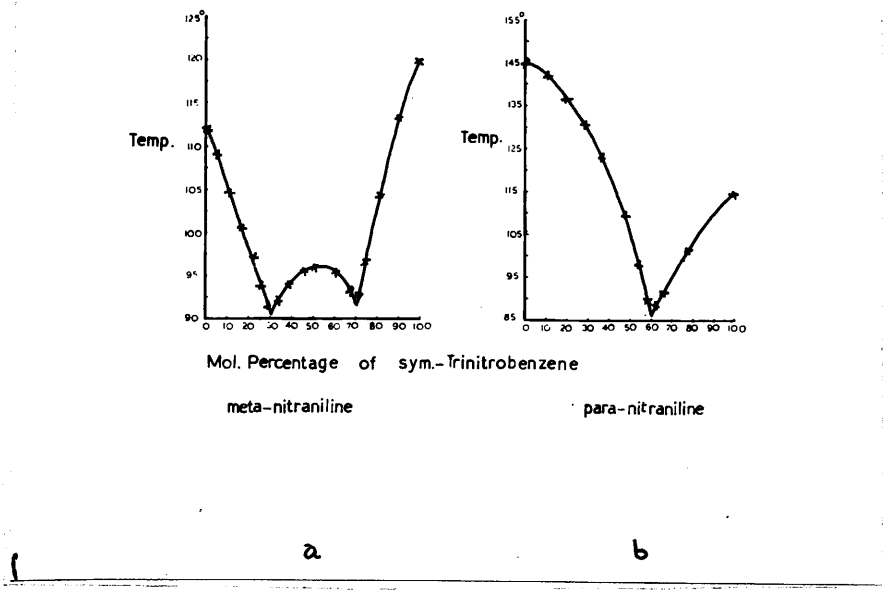
then be described by the equation

$$\underset{\text{donor}}{A} + \underset{\text{acceptor}}{B} \rightleftharpoons A^{+} B^{-}$$

Some early anomalous results of Sudborough and Beard (1910) support the opinion that para-nitraniline is a self-complex. These authors studied the complex formation of sym-trinitrobenzene with a large number of compounds including many aryl amines. They found that fairly well defined complexes were formed in many cases, including ortho- and meta-nitraniline, but not with para-nitraniline. They had graphed the melting point of a series of mixtures of the two components, against the composition of these mixtures. Whenever complex formation occurred, the type of curve shown in Fig. 12a. was obtained, but in the case of para-nitraniline, the curve was as illustrated in Fig. 12b.

The result of Fig. 12b. becomes quite clear if it is realised that the para-nitraniline molecules are already engaged in the formation of a self-complex of greater stability than that which could be formed with sym-trinitrobenzene.

Further evidence of inner molecular complex formation has been obtained from the ultra-violet absorption spectra, in the case of para-nitraniline, by Dede and Rosenberg (1934). They discovered the existance of a characteristic absorption band at about 3900Å. in all three isomeric nitranilines,



Figs. 12a and b. Types of curve obtained on studying m.pt. and composition data.

which persisted even in polar solutes. This characteristic band is quite different from those caused by the nitro-, amino- and benzene nucleus groupings, and the authors have ascribed its presence to some bond resulting from the

formation of an inner molecular complex. The absorption band was strongest for the para-compound and least for the meta-, the approximate strengths being

para: ortho: meta:: 4·2: 3·7: 3·2

A fairly close resemblence was pointed out between the inner complexes formed by the nitranilines, and the inner metallic complexes, such as copper glycollate.

Independent evidence of strong association in para-nitraniline has also been obtained from a study of the entropies of vaporization of these and other compounds, (Berliner and May, 1925; Berliner, 1928). The latent heat of vaporization varies principally with the mean square velocity of escaping molecules, and the amount of heat necessary to overcome any intermolecular attractions. The velocity may be measured by a consideration of the ratio: density of the vapour/density of the liquid, and hence the intermolecular attractions may be observed. In the case of the nitranilines and the nitrotoluenes, the molecular weights are nearly the same, and so only the intermolecular attractions may be different in these compounds.

Using Hildebrand's Law " The entropy of vaporization for normal liquids is the same when evaporated to the same concentration" , Berliner chose the arbitrary concentration of 0·00507 moles of vapour per litre. In this case, the entropy of vaporization for normal liquids is about 13·7

cals. per degree. The nitrotoluenes had the values

ortho-nitrotoluene	13·6 cals./degree
meta-nitrotoluene	14·0 cals./degree
para-nitrotoluene	13·9 cals./degree

and so all behaved as normal liquids, but in the case of the nitranilines, the following values were found

ortho-nitraniline	16·0 cals./degree
meta-nitraniline	15·7 cals./degree
para-nitraniline	17·5 cals./degree

and the comparable figures for ammonia, water and ethanol are 16·2, 16·0 and 16·7 cals./degree respectively. It may thus readily be seen that strong intermolecular attractions exist in all the nitranilines, and particularly so in the case of para-nitraniline.

Finally, the strength of the inner molecular bond is probably given a measure by the heat of formation of the crystal. The values obtained are

	m.pt.	Heat of Formation
para-nitraniline	147·5°C.	12·3 Kals./mole
meta-nitraniline	111·8°C.	6·5 Kals./mole
ortho-nitraniline	68·9°C.	6·9 Kals./mole

Experimental. The x-ray work was carried out by means of rotation, oscillation and moving film photographs with copper K_α radiation ($\lambda = 1{\cdot}54$Å.). The crystal parameters

were also independently checked by examination with precession photographs (Buerger, 1944), using Mo K_α radiation (λ = 0·7107Å.). Suitable crystals were obtained by slow growth from solution in chloroform. These were usually elongated in the direction of the b-crystal axis, and the (101) and (10$\bar{1}$) faces were frequently well developed, the former being a prominent cleavage plane; (001) was almost always well developed and when it became really broad, it appeared very similar to the yellow hexagonal plates described by Davies and Hartshorne (1934). These hexagonal plates were invariably too large for use with x-rays, and so had to be rejected.

Detailed exploration of the (0kl), (h0l) and (hk0) zones was made by moving film exposures of the equatorial layer lines for crystals rotated about the a-, b- and c-crystal axes. The multiple film technique (Robertson, 1943) was used to obtain accurate correlation between very strong and very weak reflections, the integrated intensities being obtained by careful visual estimation.

For the (0kl) zone, two crystal specimens were employed, with cross-sections 0·28 by 0·35mm. and 0·65 by 0·39mm., each about 0·80mm. in length along the a-axis. The intensity range covered was about 7000 to 1. For the (h0l) zone, the two crystals employed measured 0·18 by 0·23 mm. and 0·29 by 0·81 mm. in cross-section, and each was about 0·75mm. in length. The intensity range covered in

this zone was about 40,000 to 1, and this large range was obtained during a five hour exposure only. For the (hk0) zone, the crystals used measured 0·31 by 0·39mm. and 0·52 by 0·65mm. in cross-section, and had lengths of about 0·80mm. The intensity range for this zone was about 3600 to 1.

In all cases, the crystal was completely bathed in the x-ray beam, and only the intensities of the weaker reflections were estimated from the larger crystal specimen. Absorption corrections were not applied in view of the uniformity in cross-section of the smaller of the crystal specimens in each case.

The values of the structure factor were derived from the intensity measurements by the usual formulae for a mosaic crystal, and the results are listed in Table VI under "F measured." The calculated values of F. and the phase constants, or signs, were derived from the final co-ordinates (Table II). A composite empirical atomic scattering curve was used, derived from a careful correlation of the (h0l) calculated and observed structure factors. Individual values of f were obtained from a consideration of about 50 planes, in all of which the geometrical structure factor was greater than one-tenth of the maximum possible value. A smooth curve was then drawn to pass through the mean position of these points. The atoms were weighted in the ratio C: N: O :: 6: 6: 9. the composite atomic scattering

factors are given below

$\sin\theta$ (λ=1·54Å)	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
f	100	70	55	43	33	23	15	10	6	4	3

The numerical evaluation of the various Fourier summations was carried out by three-figure methods (Robertson 1948b). For this purpose, the a-axis was subdivided into 60 parts (interval 0·205Å.), the b-axis into 30 parts (interval 0·201Å.) and the c-axis into 60 parts (interval 0·144Å.). The positions of the contour lines were obtained by graphical interpolation from the summation totals.

TABLE VI

Measured and calculated values of the Structure Factor.

hkl	sinθ (λ=1·54)	F. meas.	F. calc.	hkl	sinθ (λ=1·54)	F. meas.	F. calc.
200	·125	23·5	-23·0	037	·741	0·5	-0·5
400	·250	1·0	1·0	038	·820	3·5	-4·5
600	·375	16·5	18·0	039	·900	2·0	-1·0
800	·500	27·5	-30·0				
10,0,0	·625	3·5	-3·5	0,3,10	·982	2·0	2·0
12,0,0	·750	<1·0	0	041	·521	8·0	1·5
14,0,0	·875	3·0	1·5	042	·544	2·0	-1·5
020	·257	19·5	-13·0	043	·581	3·5	2·0
040	·512	22·0	-23·5	044	·628	1·0	1·0
060	·767	7·0	-7·0	045	·685	13·5	2·5
002	·179	13·5	16·0	046	·747	6·5	6·5
004	·357	27·5	26·0	047	·815	1·0	2·0
006	·536	2·5	-2·5	048	·887	0·5	-0·5
008	·714	3·0	2·5	049	·961	1·5	1·5
0,0,10	·893	3·5	4·0	051	·647	1·5	1·0
				052	·665	1·5	-1·5
011	·157	30.0	28·5	053	·695	3·5	3·5
012	·223	5·0	5·0	054	·735	2·0	-0·5
013	·301	20·0	-10·0	055	·784	4·0	4·0
014	·385	12·0	12·0	056	·840	1·0	2·0
015	·472	11·0	-11·0	057	·901	1·0	1·0
016	·557	11·5	-11·5	058	·967	<1·0	-1·0
017	·647	1·0	-1·0	061	·773	<0·5	0
018	·735	1·0	-2·0	062	·789	3·0	-3·0
019	·824	1·0	1·0	063	·815	1·0	-1·0
0,1,10	·915	3·5	3·5	064	·849	3·5	-4·0
021	·271	3·0	15·0	065	·892	5·5	3·0
022	·314	5·0	6·5	066	·940	1·5	-1·5
023	·374	17·0	17·0	067	·996	0·5	0·5
024	·443	1·5	4·5	071	·901	2·0	1·0
025	·521	9·5	2·0	072	·915	1·0	-1·0
026	·600	5·0	-4·0	073	·937	<1·5	0
027	·684	1·0	-1·0	074	·967	2·0	2·0
028	·768	1·0	1·5				
029	·852	2·5	2·5	1,0,11	·994	1·0	1·0
0,2,10	·940	2·5	-2·5	109	·823	1·0	-1·0
031	·394	15·0	-18·0	107	·654	8·5	-10·0
032	·425	3·5	9·0	105	·475	26·5	-26·5
033	·471	4·5	2·0	103	·301	1·0	-2·0
034	·527	15·0	-15·0	$10\bar{1}$	·116	9·5	-7·5
035	·594	3·0	8·0	$10\bar{1}$	·109	27·0	26·0
036	·664	3·0	1·0	$10\bar{3}$	·273	10·5	7·5

hkl	sinθ (λ=1·54)	F. meas.	F. calc.
$10\bar{5}$	·453	15·5	15·0
$10\bar{7}$	·635	4·0	7·5
$10\bar{9}$	·821	1·5	-1·0
2,0,$\bar{10}$	·923	<1·0	0·5
208	·745	2·5	2·5
206	·563	15·0	-10·5
204	·394	<1·0	0
$20\bar{2}$	·225	119·0	-114 ·0
$20\bar{2}$	·212	22·5	-22·5
$20\bar{4}$	·378	4·0	0
$20\bar{6}$	·554	-9·5	-9·5
$20\bar{8}$	·728	4·0	-5·0
2,0,$\bar{10}$	·908	1·0	-0·5
309	·842	2·5	2·5
307	·668	9·0	11·0
305	·502	9·5	-10·5
303	·324	5·0	5·0
$30\bar{1}$	·211	8·5	-8·0
$30\bar{3}$	·202	25·5	30·5
$30\bar{5}$	·325	8·0	3·5
$30\bar{7}$	·653	<1·0	-1·5
$30\bar{9}$	·832	5·5	4·5
4,0,$\bar{10}$	·949	<1·0	1·0
408	·773	3·5	1·0
406	·608	1·0	-6·0
404	·445	16·0	17·0
$40\bar{2}$	·315	9·5	10·0
$40\bar{2}$	·304	2·5	-6·0
$40\bar{4}$	·428	5·5	6·0
$40\bar{6}$	·588	3·5	3·5
$40\bar{8}$	·760	4·0	2·5
4,0,$\bar{10}$	·934	1·0	-0·5
509	·884	2·0	-2·0
507	·720	4.0	4·5
505	·559	1·5	3·0
503	·442	11·5	-11·0
$50\bar{1}$	·328	26·0	-28·5
$50\bar{1}$	·409	22·5	-16·0
$50\bar{3}$	·515	8·5	-6·0
$50\bar{5}$	·648	<1·0	0·5
$50\bar{7}$	·805	21·5	-14·0
$50\bar{9}$	·864	1·0	-1·0
608	·828	1·0	3·0
606	·674	2·5	4·0
604	·531	3·0	-2·5
602	·419	<1·0	0

hkl	sinθ (λ=1·54)	F. meas.	F. calc.
$60\bar{2}$	·410	20·5	19·0
$60\bar{4}$	·514	<1·0	1·0
$60\bar{6}$	·649	5·5	-4·0
$60\bar{8}$	·805	4·0	-4·0
6,0,$\bar{10}$	·967	1·5	-1·5
709	·938	1·0	0
707	·784	1·0	-4·0
705	·638	7·5	7·5
703	·524	3·5	5·5
$70\bar{1}$	·449	10·0	12·5
$70\bar{1}$	·443	22·0	21·0
$70\bar{3}$	·510	<1·0	0
$70\bar{5}$	·618	40·5	36·0
$70\bar{7}$	·759	3·5	4·0
$70\bar{9}$	·964	5·0	4·0
808	·901	1·0	-1·0
806	·754	1·0	1·5
804	·631	5·5	5·5
$80\bar{2}$	·532	11·5	-13·5
$80\bar{2}$	·525	<1·0	0·5
$80\bar{4}$	·609	1·5	-0·5
$80\bar{6}$	·724	11·0	10·0
$80\bar{8}$	·868	1·0	-0·5
907	·863	4·5	-2·0
905	·731	1·5	3·0
903	·634	<1·0	-2·0
$90\bar{1}$	·572	15·0	-13·0
$90\bar{1}$	·564	1·0	0
$90\bar{3}$	·615	23·0	-22·5
$90\bar{5}$	·709	5·0	-5·0
$90\bar{7}$	·885	5·0	-4·5
$90\bar{9}$	·974	<1·0	0·5
10,0,8	·976	<1·0	-1·0
10,0,6	·844	5·0	-5·0
10,0,4	·735	1·5	1·5
10,0,$\bar{2}$	·652	12·5	14·5
10,0,$\bar{2}$	·645	<1·0	1·5
10,0,$\bar{4}$	·711	7·5	-7·5
10,0,$\bar{6}$	·814	4·0	3·0
10,0,$\bar{8}$	·939	1·5	1·5
11,0,7	·954	<1·0	-2·0
11,0,5	·837	1·0	0·5
11,0,3	·748	5·0	3·0
11,0,1	·696	<1·0	-2·0
11,0,$\bar{1}$	·687	2·0	1·0
11,0,$\bar{3}$	·730	2·0	1·5

hkl	sinθ (λ=1·54)	F. meas.	F. calc.
11,0,$\bar{5}$	·808	2·5	2·5
11,0,$\bar{7}$	·921	<1·0	0·5
12,0,6	·942	<1·0	1·0
12,0,4	·841	2·0	-2·5
12,0,2	·773	1·5	1·5
12,0,$\bar{2}$	·762	<1·0	1·0
12,0,$\bar{4}$	·817	2·0	-2·5
12,0,$\bar{6}$	·910	1·0	-3·0
13,0,5	·943	<1·0	-0·5
13,0,3	·864	1·0	1·5
13,0,1	·819	2·0	4·0
13,0,$\bar{1}$	·814	1·0	1·0
13,0,$\bar{3}$	·845	2·0	-2·0
13,0,$\bar{5}$	·913	3·0	0·5
14,0,4	·953	1·5	1·0
14,0,2	·898	1·0	-1·0
14,0,$\bar{2}$	·884	1·0	-0·5
14,0,$\bar{4}$	·935	2·5	2·5
15,0,3	·982	<1·0	-0·5
15,0,1	·941	<1·0	-1·0
15,0,$\bar{1}$	·935	2·5	2·5
15,0,$\bar{3}$	·968	<1·0	-0·5
110	·144	50·5	51·0
120	·264	20·0	-16·0
130	·390	25·5	-21·5
140	·566	3·5	14·5
150	·643	2·0	-1·0
160	·771	3·0	2 ·0
170	·897	1·5	2·0
210	·181	3·5	3·5
220	·285	3·0	-2·0
230	·404	18·0	20·0
240	·526	<2·0	0·5
250	·652	<2·0	2·0
260	·777	5·0	4·0
270	·902	<1·5	-1·0
310	·228	10·5	-5·5
320	·319	2·5	-2·0
330	·427	3·0	-4·5
340	·545	<2·0	-2·5
350	·667	2·0	-1·5
360	·789	<2·0	-0·5
370	·914	1·5	1·5
410	·282	31·0	-24·0
420	·358	4·5	3·5
430	·457	15·0	-15·5
440	·567	2·0	-1·0
450	·685	3·0	-3·0
460	·804	3·0	-3·0
470	·926	1·0	2·0
510	·339	4·5	10·0
520	·403	2·5	2·5
530	·494	<1·5	5·0
540	·599	<2·0	-2·5
550	·711	3·0	-6·0
560	·826	<2·0	-1·5
570	·945	<1·5	-1·0
610	·397	15·0	14·0
620	·454	16·0	16·0
630	·536	2·5	1·0
640	·634	7·5	-7·5
650	·740	7·5	4·0
660	·851	6·0	-4·5
670	·968	1·0	-1·0
710	·456	15·0	-9·0
720	·507	7·0	-7·0
730	·581	3·0	5·0
740	·672	14·0	5·0
750	·774	6·5	5·0
760	·881	7·5	4·0
770	·994	<1·0	-1·0
810	·516	6·0	-6·5
820	·561	3·0	-3·0
830	·629	11·0	10·0
840	·714	10·0	10·0
850	·810	2·0	0·5
860	·914	<1·5	0·5
910	·575	4·0	-4·0
920	·616	3·0	3·0
930	·679	<2·0	4·0
940	·759	<2·0	2·5
950	·850	2·0	-2·0
960	·948	1·5	-2·0
10,1,0	·637	2·5	1·5
10,2,0	·674	6·0	5·5
10,3,0	·731	<2·0	-1·0
10,4,0	·805	2·0	-2·0

hkl	sinθ (λ = 1·54)	F. meas.	F. calc.
10,5,0	·893	1·5	1·5
10,6,0	·987	<1·0	-1·0
11,1,0	·698	2·0	-2·5
11,2,0	·733	4·0	4·0
11,3,0	·786	<2·0	1·5
11,4,0	·856	2·0	2·0
11,5,0	·937	<1·5	0·5
12,1,0	·759	2·5	2·5
12,2,0	·790	<2·0	0
12,3,0	·840	2·5	2·5
12,4,0	·956	1·5	-0·5
12,5,0	·983	<1·0	0
13,1,0	·821	<2·0	0
13,2,0	·850	4·0	1·5
13,3,0	·897	1·5	-1·0
13,4,0	·958	<1·0	-1·0
14,1,0	·884	4·5	3·5
14,2,0	·909	3·0	-2·0
14,3,0	·953	<1·0	0·5
15,1,0	·943	<1·5	2·0
15,2,0	·969	1·5	2·0

THE CRYSTAL STRUCTURE OF NAPHTHALENE

Crystal Data. Naphthalene, $C_{10}H_8$; molecular weight, 128·2; melting point, 80·2°C; calculated density 1·172; measured density 1·152; monoclinic prismatic, $a = 8·235 \pm 0·005$, $b = 6·003 \pm 0·010$, $c = 8·658 \pm 0·010$Å., $\beta = 122°55' \pm 5'$. Absent spectra, (h0l) when h is odd; (0k0) when k is odd. Space group, C_{2h}^5 ($P2_1/a$). Two molecules per unit cell. Molecular symmetry, centre. Molecular volume, 361·7Å^3. Absorption coefficient for x-rays, $\lambda = 1·54$Å., $\mu = 0·605$ per mm. Total number of electrons per unit cell = F(000) = 136.

The crystal parameters had been measured earlier (Bragg,1921; Robertson,1933b) and were quoted as $a = 8·29$, $b = 5·97$, $c = 8·68$Å. with $\beta = 122·7°$, and it may hence be seen that these values were in very close agreement with the present more accurate parameters.

Analysis of the Structure. It had been known, ever since Sir William Bragg's pioneer work, that the crystal structure of naphthalene was very similar to that of anthracene. J.M.Robertson had given a complete determination of the latter structure in 1933, and he then proceeded to solve the naphthalene structure on the basis of the orientations found

in the case of anthracene. He then refined the co-ordinates by means of double Fourier series carried out for the zones of the three chief crystallographic axes, and expressed the final results in absolute units. With the exception of one on each of the end pairs, all the carbon atoms in the molecule were separately resolved in the combined a- and b-axis projections.

In further refinement of the atomic co-ordinates by means of triple Fourier series, it was clear that the figures given by Robertson would provide an excellent starting point, since two-dimensional methods could not give any extra resolution. Thus all possible (hkl) reflections were recorded and their intensities accurately measured visually (see experimental section), and using the phases obtained from Robertson's two-dimensional Fourier analysis, a triple Fourier series was completely evaluated giving the electron density at 54,000 points in the asymmetric unit (or 216,000 points in the unit cell), and from these figures, the atomic co-ordinates could be accurately determined.

Co-ordinates and Dimensions. The x, y and z co-ordinates of the five carbon atoms in the asymmetric unit (see Figs. 13a and b to 17a and b) were obtained with great accuracy, the individual errors in estimating the atomic centres being listed in Table VII.

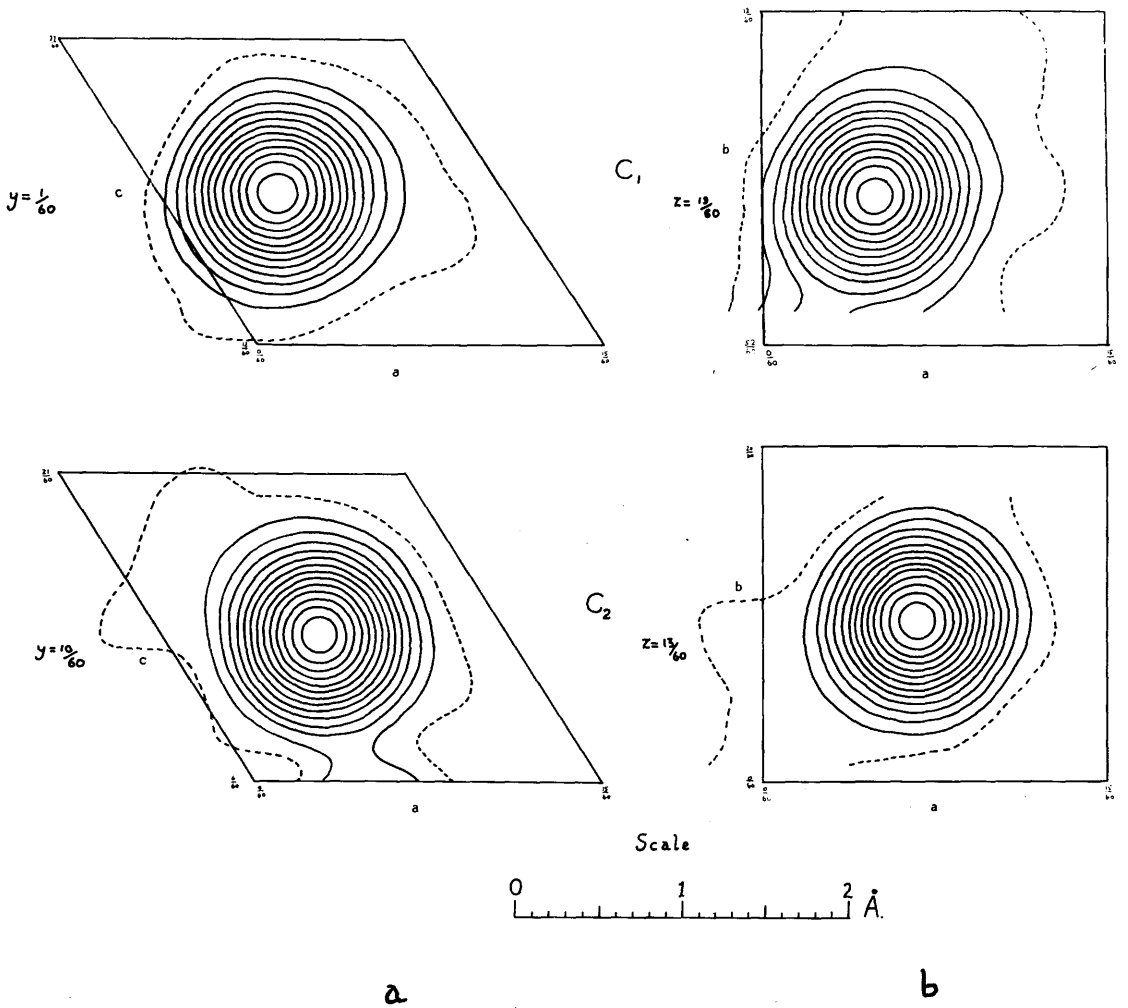


Fig. 13a and b. (upper) Sections through C_1 of the naphthalene molecule.

Fig. 14a and b. (lower) Sections through C_2 of the naphthalene molecule. In both figures, a is parallel with (010) and b is parallel with (001). Each contour line represents a density increment of one-half electron per $Å^3$, the half electron line being dotted.

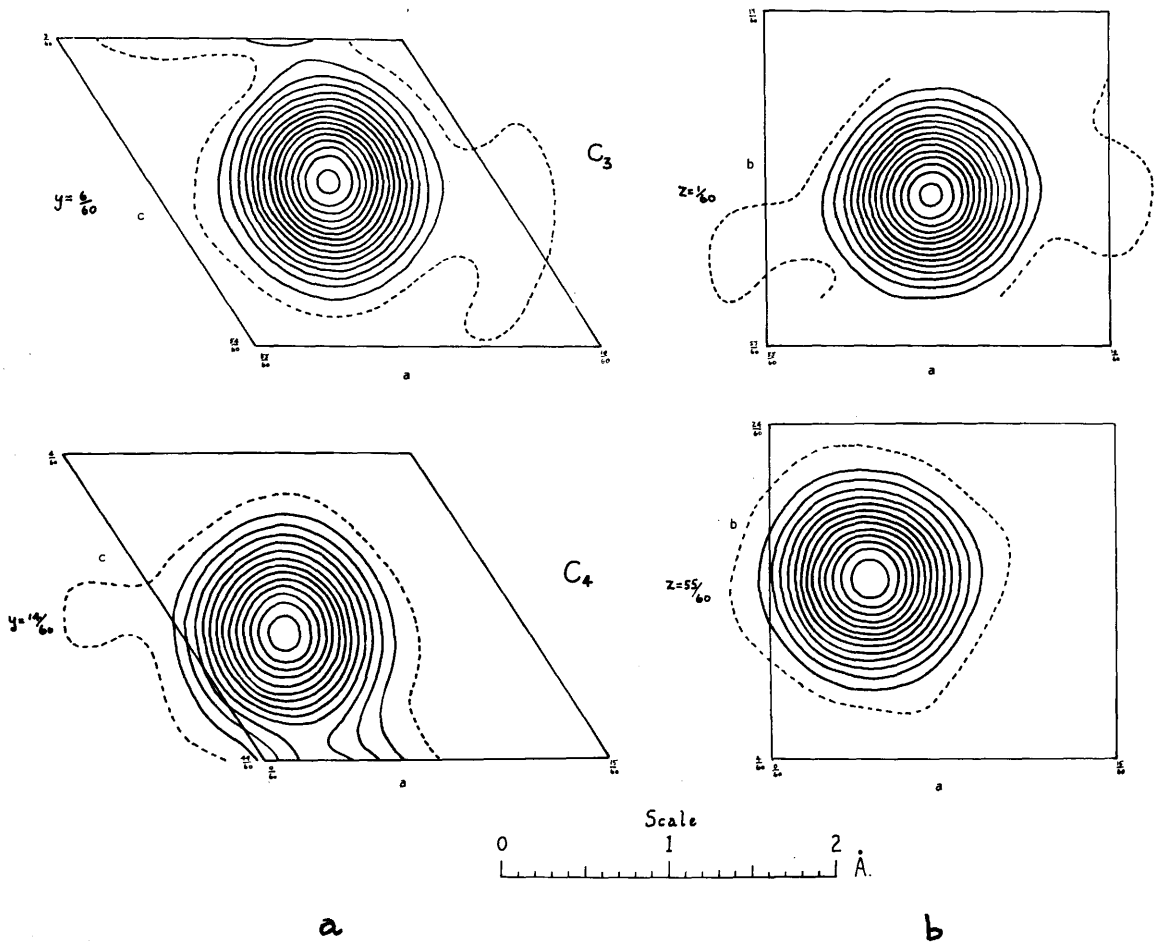


Fig. 15a and b. (upper) Sections through C_3 of the naphthalene molecule.

Fig. 16a and b. (lower) Sections through C_4 of the naphthalene molecule. In both figures, a is parallel with (010) and b is parallel with $\bar{(}001)$. Each contour line represents a density increment of one-half electron per $Å.^3$, the half electron line being dotted.

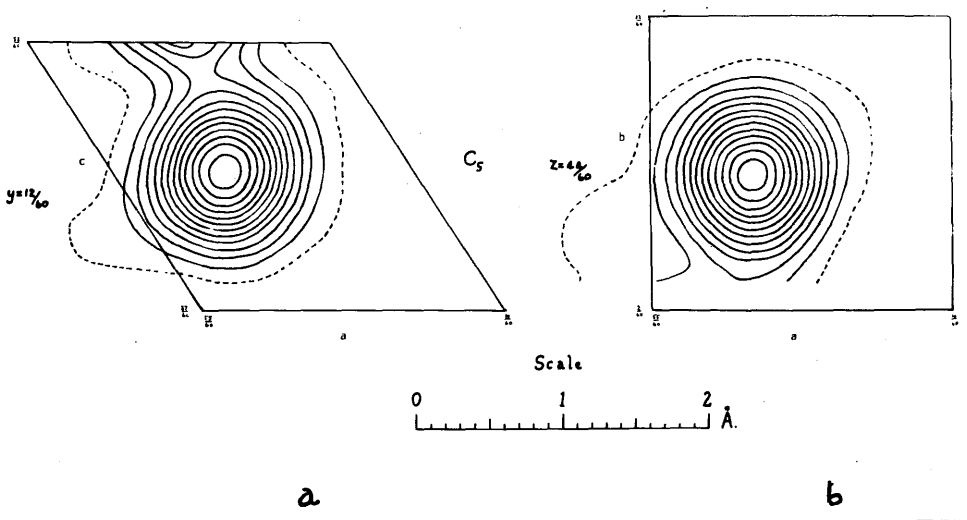


Fig. 17a and b. Sections through C_5 of the naphthalene molecule. a is parallel with (010) and b is parallel with (001). Each contour line represents a density increment of one-half electron per $Å^3$, the half electron line being dotted.

The shape of the electron contours, in all these sections, is very nearly circular, which tends to confirm the usual belief that the shape of an atom in three-dimensional space is spherical. However, an important feature, as seen in Figs. 16a and 17a is that bridges of a density of at least 2-electrons per $Å^3$ connect the atoms in this molecule,

and that the outermost levels of each atom must therefore be considerably distorted from the truly spherical.

TABLE VII

Atomic co-ordinates in Ångstrom units, with individual errors, the centre of symmetry being taken as origin.

	xÅ.	yÅ.	zÅ.
C_1	0·7156 ± 0·0044	0·0918 ± 0·0015	2·8155 ± 0·0018
C_2	0·9339 ± 0·0001	0·9602 ± 0·0031	1·8919 ± 0·0016
C_3	0·3902 ± 0·0033	0·6106 ± 0·0004	0·2969 ± 0·0014
C_4	0·6138 ± 0·0032	1·4832 ± 0·0057	-0·6847 ± 0·0035
C_5	0·0827 ± 0·0019	1·1207 ± 0·0045	-2·1945 ± 0·0032

These co-ordinates are also expressed as fractions of the axial lengths, in degrees, in Table VIII, where they are also given in terms of a set of orthogonal axes, a', b and c, in which a' is an axis chosen perpendicular to the b- and c-crystal axes. These orthogonal co-ordinates are useful for calculating interatomic distances and angles, and may be derived from the monoclinic crystal co-ordinates, by the relations

$$x' = x - z\sin 32^\circ\ 55'$$

$$z' = z\cos 32^\circ 55'.$$

TABLE VIII

	x' Å.	$\frac{2\pi x}{a}$	$\frac{2\pi y}{b}$	z' Å.	$\frac{2\pi z}{c}$
C_1	-0·8144	31·28°	5·50°	2·3630	117·00°
C_2	-0·0941	40·83	57·58	1·5890	78·68
C_3	0·2288	17·06	36·61	0·2492	12·35
C_4	0·9858	26·83	88·94	-0·5748	-28·47
C_5	1·2747	3·61	67·22	-1·8420	-91·26

These co-ordinates are listed to the fourth decimal place, and while it is true that this denotes a greater accuracy than the experimental evidence warrants, it is very useful in keeping the third decimal place accurate, and it seems very likely that this place may have some physical significance.

The atomic co-ordinates given in Tables VII and VIII lie near a mean plane, the equation of which is

$$x' - 0{\cdot}5265y + 0{\cdot}3689z' = 0$$

and the distances of the individual atoms from this mean plane are given below,

C_1	+0·0075Å.
C_2	-0·0110
C_3	-0·0007
C_4	-0·0059
C_5	+0·0044

the sign preceding each value indicating whether the atom lies nearer the origin than the plane, or whether it lies on the other side of the mean plane.

The interatomic distances and valency angles are collected in Table IX, and also in Figs. 18 and 19. The average error in bond lengths may be assumed to be not greater than 0·010Å.

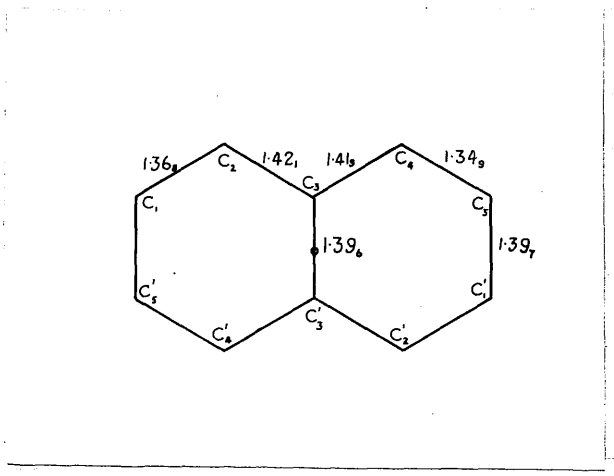


Fig. 18. Measured bond lengths in the naphthalene molecule.

It may thus be seen that the central bond, which had earlier been supposed to be somewhat longer than normal, is in fact, very close to the standard value of 1·39Å. for the carbon-carbon distance in the aromatic ring. The chemically reactive linkage in the " αβ" position is

distinctly shorter, at $1{\cdot}36_8$ and $1{\cdot}34_9$ Å., while the $C_2 - C_3$ link is somewhat longer than usual, at $1{\cdot}42_1$ and $1{\cdot}41_9$ Å. The "outside" bond, $C_1 - C_5'$, is found to be almost the identical length as the central bond, at $1{\cdot}39_7$ Å. The hexagonal angles are all very close to the regular value of 120°, and it thus appears that irregularities in the lengths of the sides of the aromatic ring do not greatly affect the internal angles.

TABLE IX

Interatomic distances and valency angles.

$C_1 - C_2 \cdots 1{\cdot}36_8$ Å.	$C_2 - C_5' \cdots 2{\cdot}40_5$ Å.
$C_2 - C_3 \cdots 1{\cdot}42_1$	$C_1 - C_3 \cdots 2{\cdot}41_3$
$C_3 - C_4 \cdots 1{\cdot}41_9$	$C_2 - C_3' \cdots 2{\cdot}42_1$
$C_4 - C_5 \cdots 1{\cdot}34_9$	$C_4 - C_1' \cdots 2{\cdot}38_8$
$C_1 - C_5' \cdots 1{\cdot}39_7$	$C_5 - C_3 \cdots 2{\cdot}39_3$
$C_3 - C_3' \cdots 1{\cdot}39_6$	$C_4 - C_3' \cdots 2{\cdot}44_2$
$C_2 - C_4' \cdots 2{\cdot}79_1$	

$C_2\hat{C}_1C_5' \cdots 120°52'$	$C_3'\hat{C}_3C_4 \cdots 120°21'$
$C_1\hat{C}_2C_3 \cdots 119°48'$	$C^3\hat{C}^4C^5 \cdots 119°38'$
$C_2\hat{C}_3C_3' \cdots 118°31'$	$C_4\hat{C}_5C_1' \cdots 120°43'$

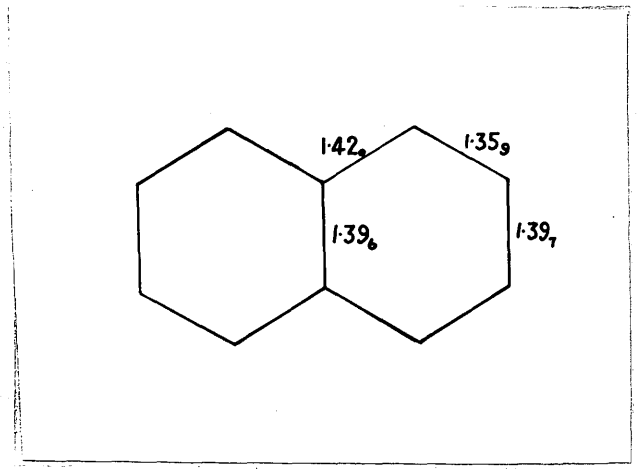


Fig. 19. Averaged observed bond lengths in naphthalene.

Electron Distribution. It had been noticed in anthracene (Robertson, 1933a) that the electron density varied throughout the molecule, being highest for the atoms in the "meso"-positions and least for the atoms in the "benz"-positions. The early structural determination of naphthalene, on the other hand, did not show any such observable differences. In the present structure, where every atom is completely resolved, such a difference has become very noticeable. The carbon atoms which form the central link have the highest electron density, with about 8·0 electrons per cubic

Ångstrom unit, and this value falls to between 7·0 and 7·5 electrons for the atoms C_2 and C_4, and the outermost atoms, C_1 and C_5 have densities of between 6·5 and 7·0 electrons per cubic Ångstrom unit.

Similar variations in electron density have been observed in many aromatic hydrocarbons, and there seems to be no doubt that this effect is closely related to the chemistry of the molecule. It would be a very difficult task to interpret these variations in the cases of the more complex substances, but the wave-mechanical equation for the naphthalene molecule, although also very complicated, shows greater promise of solution. An attempt at such a solution will be undertaken in this laboratory, for if it is successful, it should shed a great deal of light on the chemistry of the polycyclic aromatic hydrocarbons.

Discussion. A full discussion cannot be undertaken at this stage in the analysis, and will require to await the results of computing the electron densities in the mean plane that passes through the whole molecule. This will then enable the exact electron densities at the peaks of each atom to be estimated, and also the electron distribution between atomic centres, for it has already become apparent that the electron density there does not fall off to zero,

but remains at a height of about two electrons per cubic Ångstrom unit.

A series of calculations designed to give an accurate theoretical treatment of the naphthalene molecule have already been completed. The simplest of these is obtained by a consideration of the possible Kekulé structures for the naphthalene molecule. This enables the amount of double bond character in each linkage to be estimated, and using a simple curve (Pauling, 1942) which gives a relationship between interatomic distances and the amount of double bond character in a single bond-double bond resonance system for carbon-carbon, the bond lengths may be obtained. The results of such a calculation are shown in Fig. 20.

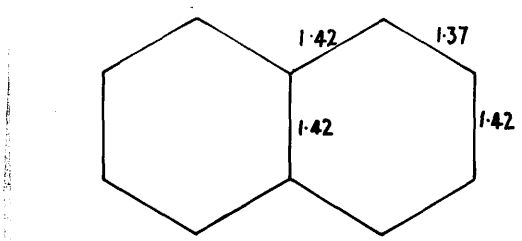


Fig. 20. Calculated bond lengths in naphthalene, on the basis of the Kekulé structures.

One of the first of the more elaborate treatments (Sherman, 1934) was based upon the possible forty-two canonical (linearly independent) structures which may be written for naphthalene. This required the setting up of a secular equation of the forty-second degree, in the same manner as did Pauling and Wheland (1933), but Sherman attempted a more rigorous solution. He regarded the molecule as a ten-electron system with spin degeneracy only, and was able to break the large equation down into a number of simpler factors, for the symmetry of the molecule allows a sixteenth, a fourteenth and two sixth-degree factors. The structures considered involved three which were unexcited, sixteen singly excited, twenty doubly excited and three triply excited. These simplifications enabled the evaluation of the coefficients of the wave-function, and hence the energy of each bond.

The coefficients thus obtained were then used (Pauling, Brockway and Beach, 1935) to calculate the interatomic distances in the molecule. These results are given in Fig. 21.

An essentially similar approach was made by Penney (1937), in which the electron pair method was employed, for in both cases, the treatment was from the point of view of a problem in resonance energies. This calculation neglected the doubly- and triply-excited structures, and hence

was able to approximate to the energy required in the ground state, from which, the order of the interatomic linkages could be found. These orders of linkage led to the bond distances given in Fig. 22.

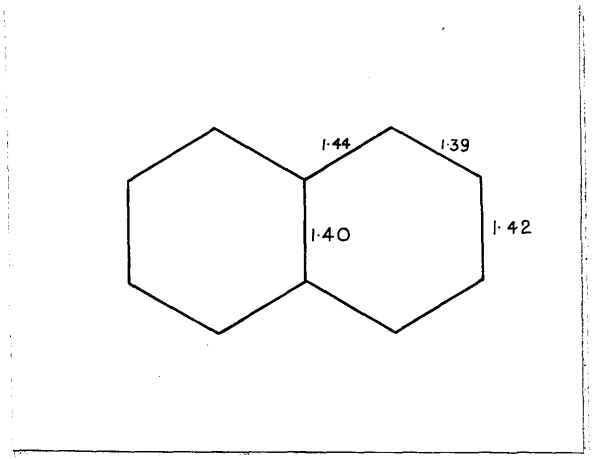


Fig. 21. Calculated bond lengths in naphthalene (Pauling, Brockway and Beach, 1935).

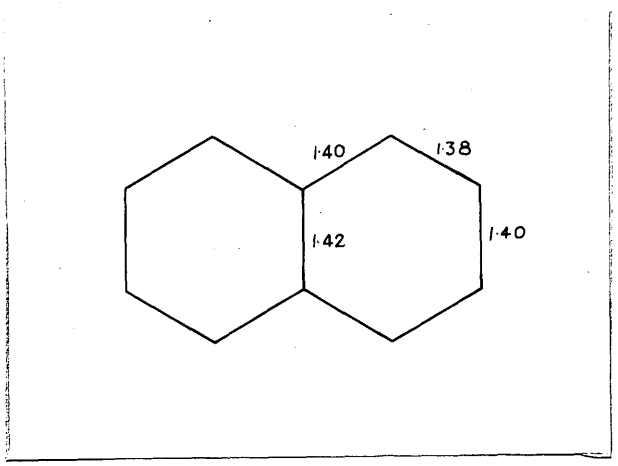


Fig. 22. Calculated bond lengths in naphthalene (Penney, 1937).

A somewhat different treatment was offered by Lennard-Jones and Coulson (1939), in which the motion of the mobile electrons was primarily considered. This method still depended upon calculating the bond order, and derived the bond length from this by means of an empirical curve (different from Pauling's) which related the order and length of the carbon-carbon bond. The results obtained by this method are given in Fig. 23.

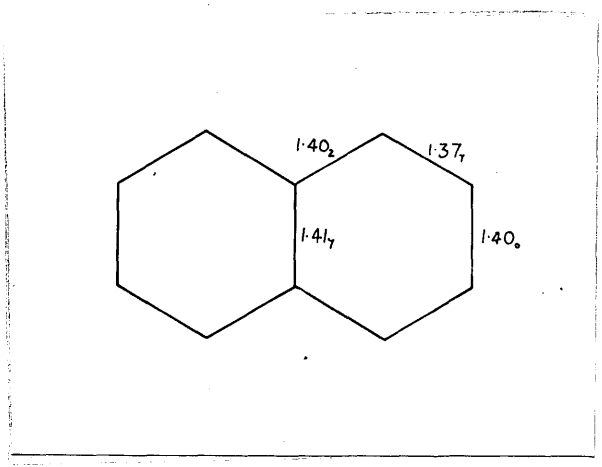


Fig. 23. Calculated bond lengths in naphthalene (Lennard-Jones and Coulson, 1939)

This treatment gives results very similar to those of Penney, but the differences, although slight, bring the values closer to the experimental figures (Figs. 18 and 19). Thus, although quite good agreement has been obtained by these various treatments, the results given by the simple Kekulé approach are just as reliable. It would hence seem

that unless the original canonical equation of the forty-second degree is rigorously solved, with no simplifying assumptions, the labour required for the semi-solutions is largely wasted.

From the purely chemical point of view, the observed variations in the bond lengths are of great interest. It is well known that in chemical reactions, the points at which the naphthalene molecule permits substitution with the greatest ease are in the α- and β-positions, corresponding to atoms C_1 and C_2 or C_4 and C_5 in Fig. 18. These "αβ" bonds, which are distinctly shorter at $1{\cdot}36_8$ and $1{\cdot}34_9$ Å., than the other linkages, may hence be considered to possess a greater amount of double bond character, and therefore more electron material, which is in keeping with the modern theory of substitution in the aromatic nucleus. The difference between these two distances $C_1 - C_2$ and $C_4 - C_5$, of 0·019Å., is just on the probable limits of error, for if each bond is of length $1{\cdot}35_8$Å., the error in the two observed values will be ± 0·009Å. and hence the difference may not have any physical significance. Indeed, it would seem most unlikely that the two ring systems in naphthalene could be different.

In the same way, the divergences of the atomic centres from the mean plane are also just on the limits of probable error. However, Fig. 24. shows, in greatly exaggerated

form, that the mutual arrangement of the carbon atoms is such as to give a puckered effect, and it may be that this effect is not entirely coincidental.

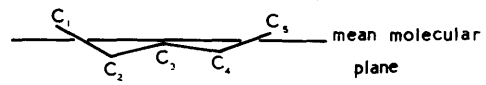


Fig. 24. End-on view of the naphthalene molecule.

In the absence, as yet, of a complete theoretical solution for the naphthalene wave-equation, it will be necessary to wait until the accurate atomic co-ordinates of anthracene, which is being studied in a parallel investigation, are obtained. If this molecule should evince a similar puckered effect, then the divergences should be considered as real.

Experimental Section.

Preservation of Crystal Specimen. Single crystals of naphthalene are so volatile that, placed in the open, they generally disappear within the space of an hour or two. It thus became imperative to evolve a method which would effectively preserve a single crystal for a period of up to two weeks. Several of the well known methods were tried, and

for a variety of reasons, rejected. The method finally used employed thin gelatin capsules, 15·5mm. in length and 5·5mm. in diameter. These capsules,(size 2 and manufactured by Messrs. Park, Davis and Co., Detroit, U.S.A.), were very uniform in thickness (0·12mm.) and possessed considerable mechanical strength. The naphthalene crystal was mounted in the usual way, and after the mounting agent had hardened, some powdered naphthalene was pressed into the base (Apiezon Sealing Compound Q was found to be very suitable) and the crystal and powder enclosed by a capsule which was pressed well down into the base (see Fig. 25.)

Fig. 25. Mounted naphthalene crystal, completely sealed off.

A suitable seal was then made by painting some gum over the gelatin-plasticine boundary. The vapour pressure then set up inside the capsule by the powdered naphthalene was found to be sufficient to prevent any undue volatilization.

Recording (hkl) Reflections. The method used was to explore all the possible layer lines associated with a selected axis by means of an equi-inclination Weissenberg camera. The camera employed was built in the departmental workshop, to Professor Robertson's specifications. The maximum equi-inclination angle that could be obtained with this set-up was 28°, corresponding to about the fourth layer line of a zone associated with an axial length of 8Å.

Measurement of Intensities. The various zones (see Table X) were explored in detail by moving film exposures of the n-layer lines, for crystals mounted about suitable axes, using copper K_α radiation ($\lambda = 1{\cdot}54$Å.). The multiple film technique (Robertson, 1943) was used to correlate the very strong and very weak reflections. The film employed was Kodak Industrex Type-D, and while the ratio in which the intensity of the x-ray beam is diminished from film to film was accurately known in the case of Ilford film (2·3), the corresponding ratio for the Kodak film was not known. This

Kodak film was used because of the greater contrast. The ratio was found in two ways, (1) by printing calibrated wedges of varying time lengths on to a set of three films, and (2) by comparison of a set of diffracted spectra produced by a given crystal and recorded both on Ilford and Kodak film. The mean value for the film to film ratio thus obtained was 5·1. This value was later confirmed by the research department at Messrs. Kodak, where they used two different methods, (3) micro-densitometer tracings on the diffraction pattern on two super-imposed films, and (4) by measuring the film absorption directly with an ionisation chamber. In all these cases, the films are separated from each other by two thicknesses of black paper.

The intensities of the various reflections were all carefully estimated visually. There are two principal methods used in visual intensity estimations, a) in which a fairly weak spot on the strongest film is taken as unity, from which other spots on the same film of strength up to thrice this may be estimated; the film ratio then enabling all other spots to be determined in terms of these, and b) in which one of the strongest spots on the strongest film is given a value of 1000, and by similarly working downwards, evaluating the strengths of all the other reflections.

To some extent, these two methods are complementary, and the visual estimates of the naphthalene reflections were

obtained by both methods, and the average value was taken as correct. In general, the intensities found by the two methods, each being used by a different researcher, were found to agree within 10% of each other, and this lent great confidence to the subsequent work. The maximum range of intensities recorded was 5,300 to 1, in the (hll) zone, but usually a range of not more than 1000 to 1 was found.

635 planes out of a possible 830 were observed.

Corrections applied. The absorption of x-rays ($\lambda = 1{\cdot}54$Å.) by naphthalene is 0·605 per mm., and while this is not large, in view of the general accuracy required for this structural determination, absorption corrections were applied. These were worked out graphically, from which the mean path of the x-ray beam, for each reflection through the crystal, could be obtained. These values of μ and t, known for each plane, could then be substituted in the relation

$$I = I_o e^{-\mu t},$$

where I_o was the observed intensity, t the mean path through the crystal, and μ was the coefficient of absorption. Thus, the corrected intensities only were used in evaluating the structure factor. The value of $e^{-\mu t}$ varied between 1·22 and 1·55. In the cases where some strong planes showed signs of extinction, where several values of the intensity

were available, the highest one was chosen.

The usual Lorenz and polarisation factors were also applied, but the Cox and Shaw (1930) factor for n-layer reflections had to be replaced by a new factor (Tunell, 1939) since an equi-inclination camera was employed. This factor is of the form

$$D_e = \frac{\cos^2\mu - \cos^2\theta}{\sin\theta}$$

where μ is the equi-inclination angle, and θ is the Bragg reflection angle.

Crystal zones and crystal sizes. A consideration of the reciprocal sphere of naphthalene showed that all possible (hkl) planes could be recorded if the (hn$\bar{1}$), (nk$\bar{1}$), and (h,h±n,$\bar{1}$) zones were fully investigated, where n = 0, 1, 2, 3, and 4.

The zones examined, in detail, together with the dimensions of the crystal giving that zone of reflection, are listed in Table X.

TABLE X

Zone examined and size of crystal employed.

Zone	Crystal Dimensions
h0$\bar{1}$ h1$\bar{1}$ h2$\bar{1}$	·31 × ·71 × ·95 mm.
h3$\bar{1}$	·28 × ·61 × ·90
0k$\bar{1}$ 1k$\bar{1}$	·13 × ·39 × ·39
1k$\bar{1}$ 2k$\bar{1}$ 3k$\bar{1}$	·24 × ·53 × ·79
h,h,$\bar{1}$ h,h±1,$\bar{1}$ h,h±2,$\bar{1}$	·26 × ·61 × 1·00
h,h±3,$\bar{1}$ h,h±4,$\bar{1}$	
h,h±1,$\bar{1}$ h,h±2,$\bar{1}$	·31 × ·53 × 1·20

In all these cases, the dimensions given are the cross-section multiplied by the length of the crystal.

Correlation of Relative Structure Factors. The relative structure factors for each zone were first worked out, using all the appropriate correction factors (see pages 90 to 91). The values for the (h0l) structure factors obtained by Robertson, on the absolute scale, were taken as standard, so that the new (h0l) set could at once be placed on the

same scale. Then, the (h, h, $\underline{1}$), (h, h±2, $\underline{1}$) and (h, h±4, $\underline{1}$) sets of planes could be placed on a common scale by virtue of the (11$\underline{1}$), (22$\underline{1}$), (13$\underline{1}$) and (31$\underline{1}$) planes which occur in several of these zones. These three zones, now all on one scale, further have many (h0l) planes among them, and so by means of these planes, all three zones could be placed on the (h0l), and hence, the absolute scale.

Next, (h1$\underline{1}$) could be placed upon the absolute scale, by virtue of the (11$\underline{1}$), (31$\underline{1}$) and (51$\underline{1}$) planes already on the absolute scale, and similarly, so could (h2$\underline{1}$) and (h3$\underline{1}$). It was now a simple matter to place the remaining zones on the absolute scale, because of the large number of planes in common already on that scale.

The final values chosen for the structure factors (see Table XI) were the average of the various values so obtained, for each plane frequently occurred in different zones. Where the plane was associated with a very large intensity, the highest value was adopted, in view of the possibilities of extinction. In one case, (110), where Robertson's value was considerably higher (and his had been obtained by the use of an ionisation chamber), his value was adopted.

Constancy of Discrepancy between Planes Common to Several Zones. In this correlation process, it was very frequently found that of a dozen or more (in some cases, up to fifty) planes common to several zones, if the structure factors on the absolute scale were compared by means of the relation

$$\Delta = \frac{\Sigma|F'obs. - F''obs.|}{\Sigma|F'obs.|}$$

(where F'obs. was the value of the structure factor from one zone and F''obs. was the value of the same plane from another zone), that Δ always had a value of about 10% to 11%. Rarely Δ became as low as 8·7%, and it never became greater than 11·2%.

This constancy of discrepancy was clearly a function of the extinction, for the average values of the intensities were sufficiently good to give Fobs. to within 5% of their correct figures.

Calculation of the Geometrical Structure Factor. For the space group $P2_1/a$, the geometrical structure factor has the form

$$S = 4\cos 2\pi\left(\frac{hx}{a} + \frac{lz}{c} + \frac{bh+ak}{4ab}\right).\cos 2\pi\left(\frac{ky}{b} - \frac{bh+ak}{4ab}\right) \quad (6)$$

and this may be rewritten to give

$$S = 4\cos 2\pi\left(\frac{hx}{a} + \frac{lz}{c}\right).\cos 2\pi\left(\frac{ky}{b}\right) \text{ for } h + k = 2n \quad \text{____(7)}$$

and,

$$S = -4\sin 2\pi\left(\frac{hx}{a} + \frac{lz}{c}\right).\sin 2\pi\left(\frac{ky}{b}\right) \text{ for } h + k = 2n+1 \quad \text{___(8)}$$

To simplify these calculations, all the angles of the form $h\theta_1 \pm l\theta_3$ were tabulated, where $\theta_1 = \frac{x}{a}$, $\theta_2 = \frac{z}{c}$, and the corresponding sines and cosines of these angles evaluated; and similarly for $k\theta_2$, when it then became possible to determine the 830 geometrical structure factors by plain substitution in (7) and (8) and summing over the five atoms for each plane. The maximum possible value for S is when $\theta_1 = \theta_2 = \theta_3 = 0°$, and hence is 5, and each Scalc. was expressed as a fraction of this maximum value.

Atomic Scattering Factor. The original empirical curve derived from anthracene (Robertson, 1933a) was used in the calculation, for it would not affect any phase, although it did not give a very satisfactory fit.

Numerical Evaluation of the Triple Fourier Series. The total time required to perform the numerical summation of a full triple Fourier series, using the Robertson stencil method, and a simple adding machine, has been estimated at about forty weeks of continuous application. In view of this great amount of purely mechanical labour, the summation

has been carried out on a Hollerith International Business Machine by the Scientific Computing Service, London. This machine is the same one as that employed to sum the electron density along selected sections in penicillin.

The unit cell has had each edge divided into sixty parts, and the fraction summed was over one complete asymmetric unit, in which $\underline{x}$ had the values 0 to 30/60, $\underline{y}$ from 0 to 30/60 and $\underline{z}$ from 0 to 60/60 . The interval was 0·1373Å. for the a-axis, 0·1002Å. for the b-axis and 0·1443Å. for the c-axis.

The operation of evaluating the triple summation was then proceeded with as follows;

The general expression

$$\rho(x,y,z) = \frac{1}{V} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} |F(hkl)| \cos 2\pi \left\{ h\underline{x} + k\underline{y} + l\underline{z} \right\}$$

may be reduced to

$$\begin{aligned}\rho(x,y,z) = \frac{4}{V} \sum_{\circ}^{\infty} \sum_{\circ}^{\infty} \sum_{\circ}^{\infty} \Big\{ & \Big[F(hkl) + F(hk\bar{l}) \Big] \cos 2\pi h\underline{x} \cdot \cos 2\pi k\underline{y} \cdot \cos 2\pi l\underline{z} \\ & + \Big[F(hk\bar{l}) - F(hkl) \Big] \sin 2\pi h\underline{x} \cdot \sin 2\pi k\underline{y} \cdot \sin 2\pi l\underline{z} \\ & \qquad \text{for } h + k \text{ even} \\ & - \Big[F(hkl) + F(hk\bar{l}) \Big] \sin 2\pi h\underline{x} \sin 2\pi k\underline{y} \sin 2\pi l\underline{z} \\ & + \Big[F(hk\bar{l}) - F(hkl) \Big] \cos 2\pi h\underline{x} \cos 2\pi k\underline{y} \cos 2\pi l\underline{z} \Big\} \\ & \qquad \text{for } h + k \text{ odd.}\end{aligned}$$

which is the most convenient form for the Hollerith scheme. The sums and differences of the structure factors, for $\underline{l}$ positive and negative, which have to be introduced into this expression are then obtained from a consideration of the multiplicities of the various terms. These are as follows;

F(hkl)	4	if $F(hk\bar{l})$ is given
F(0kl)	4	if $F(0k\bar{l})$ is not given
F(hk0)	4	
F(0k0)	2	
F(00l)	2	if $F(00\bar{l})$ is not given
F(h0l)	2	if $F(h0\bar{l})$ is given
F(h00)	2	
F(000)	1	

and hence for all values of $\underline{l}$, the following sums may be formed;

	$\underline{h}$ even	$\underline{h}$ odd
for k = 0	$2\left[F(h0l)+F(h0\bar{l})\right]$	
	$2\left[F(h0\bar{l})-F(h0l)\right]$	not required for k = 0
for k > 0 and even	$4\left[F(hkl)+F(hk\bar{l})\right]$	$-4\left[F(hkl)+F(hk\bar{l})\right]$
	$4\left[F(hk\bar{l})-F(hkl)\right]$	$4\left[F(hk\bar{l})-F(hkl)\right]$
	$2\left[F(0k0)\right]$	
for k > 0 and odd	$-4\left[F(hkl)+F(hk\bar{l})\right]$	$4\left[F(hkl)+F(hk\bar{l})\right]$
	$4\left[F(hk\bar{l})-F(hkl)\right]$	$4\left[F(hk\bar{l})-F(hkl)\right]$

and in this manner, the experimental set of structure factors

suitably presented so as to give the final electron density figures in terms of 1000 = 1 electron per cubic Ångstrom unit, could be combined among themselves to give a new set of factors, F'. These F' terms are then recorded on special sheets from which the first Hollerith cards are punched. These cards also contain the magnitude and sign of the F' term, as well as its appropriate hkl index. The cards are then passed through the tabulator, associated with a set of detail cards(which contain the information peculiar to any special function) whereupon $\sum h \left\{ \begin{matrix} \cos \\ \sin \end{matrix} \right\} 2\pi h \frac{x}{a}$ is recorded for the given range of x. These values are then copied on to a new set of cards, when the process of summing over y is performed in a like manner , and so finally, the summation is extended over l as well.

The final figures were so adjusted that three figures were printed, in general, for the electron density at each point, and a fourth figure also appeared in the margin of the sheet. This extra figure ensured a constant three place accuracy in the final summation, and so, for example, at a carbon peak where the electron density was given as 6824, it could be said that 6·82 electrons per cubic Ångstrom unit was an accurate assessment of the density of electron material at that point.

Graphical Interpretation of the Electron Density values.

The results of the three-dimensional summation by the Hollerith machine were given in the form of 264 sheets of figures, each sheet containing 297 points at which the electron density had been computed. To obtain accurate values for the atomic co-ordinates, as well as to investigate the shapes of the atoms and also the electron distribution between atomic centres, it was necessary to draw sections parallel with the a-axis, through all points of density greater than 0·5 electrons per cubic Ångstrom unit. A very encouraging sign in this work was that the general level of the electron background was most uniform, and lay between zero and 0·5 electrons, with only very occasional negative patches.

The actual labour involved in drawing these sections accurately, on the scale of 10cm. to the Ångstrom unit, was very considerable.

These sections then enabled the electron densities on two-dimensional slices through the atoms to be drawn. In this manner, four slices parallel to (010), and four slices parallel to (001), passing near the atomic centre, were constructed. The centres of each of the sets of four slices were then separately estimated visually, and hence, the atomic co-ordinates, in terms of the cell side, were obtained by reference to the nearest cell division, so that only a very

small direct measurement was required. These co-ordinates were then averaged, and are collected in Table VII.

TABLE XI

Magnitudes and Signs of F(hkl)

(h0l) (k = 0)

		h					
		0	2	4	6	8	10
	9	-					
	8	-1·3					
	7	-3·9	-2·6				
	6	-2·7	-3·4	-1·3			
	5	-1·6	-1·1	1·2			
	4	16·5	6·1	-	0·9		
	3	22·4	16·8	1·7	-4·3		
	2	-18·2	5·5	5·7	-1·9		
	1	33·5	-4·9	-1·2	-	-	
l	0	136·0	43·9	-4·6	-6·2	-1·3	
	$\bar{1}$		37·5	2·9	-8·7	-5·7	
	$\bar{2}$		-17·3	-6·2	-3·6	-3·3	
	$\bar{3}$		0·6	1·0	3·3	1·8	-
	$\bar{4}$		8·7	9·4	11·7	6·3	-
	$\bar{5}$		-3·2	-3·9	3·9	6·1	-
	$\bar{6}$		1·2	1·0	-1·9	-	-
	$\bar{7}$		3·5	13·3	11·2	1·9	-
	$\bar{8}$		-1·5	6·6	12·3	6·5	-
	$\bar{9}$		-	-2·2	-	1·2	
	$\bar{10}$		1·8	2·2	-1·4	-1·4	
	$\bar{11}$			-	2·1		

(h1$\underline{1}$) (k = 1)

	l	h = 0	1	2	3	4	5
	8	-0·7	0·7				
	7	-3·5	-2·0	0·9	-0·7		
	6	-4·1	0·9	0·9	-1·1	-	
	5	1·4	1·0	1·0	0·9	0·9	-
	4	9·4	2·9	-2·2	-2·0	-3·0	-1·4
	3	6·7	11·3	-4·0	3·2	-8·0	-2·0
	2	3·8	-3·3	2·2	5·0	-3·4	1·5
	1	6·4	-8·9	-1·3	-6·5	1·0	1·1
$\underline{1}$	0		37·0	-28·9	5·4	-14·4	-4·7
	$\overline{1}$		19·5	-28·1	20·3	-23·5	3·0
	$\overline{2}$		-12·6	1·1	0·6	-3·0	3·5
	$\overline{3}$		14·8	6·9	-6·9	11·7	1·6
	$\overline{4}$		12·2	-10·0	15·7	5·0	10·2
	$\overline{5}$		1·0	-6·2	-1·5	-2·5	1·9
	$\overline{6}$		5·4	8·4	2·5	2·9	-1·4
	$\overline{7}$		1·3	10·2	8·0	8·4	7·1
	$\overline{8}$		-1·9	2·2	-	3·9	5·0
	$\overline{9}$		0·8	-1·1	-1·0	-0·9	-2·5
	$\overline{10}$			0·9	1·5	-0·7	0·7
	$\overline{11}$						-

(hl$\underline{1}$) (k = 1) continued.

		h = 6	7	8	9	10
	8					
	7					
	6					
	5					
	4	-				
	3	-4·3	-			
	2	-4·4	-1·3			
	1	0·8	0·8	-		
$\underline{1}$	0	-1·6	-1·3	-		
	$\bar{1}$	-6·1	-2·6	-	-2·6	
	$\bar{2}$	-1·1	1·0	0·9	-0·9	
	$\bar{3}$	3·6	-	-	-0·8	0·8
	$\bar{4}$	2·7	2·7	-2·3	-	-2·9
	$\bar{5}$	1·0	2·9	-1·8	0·9	-3·0
	$\bar{6}$	-	-1·9	-	-	-
	$\bar{7}$	-1·2	1·7	-2·6	-	-
	$\bar{8}$	-1·4	5·5	-5·2	1·5	-2·7
	$\bar{9}$	-0·9	0·8	-2·3	1·4	
	$\bar{10}$	-	-0·7	0·6	-0·7	
	$\bar{11}$	-	-			

(h2$\underline{1}$) (k = 2)

		h					
		0	1	2	3	4	5
	9	-					
	8	-0·9	0·6				
	7	2·5	-1·7	-	-0·7		
	6	8·2	-3·9	3·8	-	-	
	5	1·4	-4·2	1·3	-1·6	0·7	0·7
	4	-4·0	-4·5	-8·4	-5·6	-4·3	-1·5
	3	11·2	-4·0	-2·2	-6·9	-3·8	-4·9
	2	5·3	-1·5	3·1	1·3	1·8	-3·4
	1	-15·8	-7·5	-11·5	0·8	-2·8	1·8
$\underline{1}$	0	-14·7	-13·2	-6·9	-15·0	-2·3	-3·1
	$\overline{1}$		-2·3	4·0	-15·1	14·2	-14·3
	$\overline{2}$		11·8	1·9	2·7	7·0	-6·4
	$\overline{3}$		9·2	16·3	8·3	1·5	1·0
	$\overline{4}$		-1·2	12·2	-2·3	10·0	-1·4
	$\overline{5}$		-1·2	1·1	-6·9	4·6	-5·1
	$\overline{6}$		7·8	4·9	2·2	-1·4	-2·0
	$\overline{7}$		6·2	4·6	6·5	-	1·3
	$\overline{8}$		1·0	-2·5	2·0	-2·7	1·6
	$\overline{9}$		-1·4	1·3	-0·6	-1·3	-
	$\overline{10}$			0·6	0·9	1·1	1·0

(h2$\underline{1}$) (k = 2) continued.

		h = 6	7	8	9	10
	9					
	8					
	7					
	6					
	5					
	4	-				
	3	-0·8				
	2	-	-2·0			
	1	1·5	-	1·1		
$\underline{1}$	0	-	-	-1·1		
	$\bar{1}$	7·7	-3·5	-	-0·8	
	$\bar{2}$	8·3	-4·2	2·1	-	
	$\bar{3}$	-3·3	-2·9	-2·8	-1·3	
	$\bar{4}$	-1·7	-3·6	-4·8	-4·8	-3·0
	$\bar{5}$	3·2	-2·2	-	-2·6	-
	$\bar{6}$	-1·6	-1·5	-	-	-
	$\bar{7}$	-2·4	-2·2	-1·5	-	-
	$\bar{8}$	-1·9	-2·5	-	-3·3	-
	$\bar{9}$	-1·1	1·3	-	-0·8	
	$\bar{10}$	2·0	2·0	-		

$(h\bar{3}\bar{1})$ $(k = 3)$

		h					
		0	1	2	3	4	5
	8	-	-				
	7	-1·3	-0·6	-1·0			
	6	-3·2	5·8	-3·3	2·1		
	5	-6·8	-1·1	-5·5	3·4	-1·4	
	4	-8·9	-9·8	-6·1	-4·0	-1·4	-
	3	-7·8	3·0	-5·7	-3·0	-2·0	-0·5
	2	-8·0	10·8	-4·6	4·5	-1·5	0·8
	1	-13·7	-6·5	-5·3	-0·9	-	-1·1
$\underline{1}$	0		-10·0	1·6	-4·3	-	-1·1
	$\bar{1}$		-8·9	9·7	0·8	1·0	5·3
	$\bar{2}$		0·6	5·4	-5·6	-0·8	1·3
	$\bar{3}$		8·8	0·8	-1·8	-5·5	-8·9
	$\bar{4}$		-5·2	2·9	2·0	-4·8	-0·7
	$\bar{5}$		-7·8	2·7	-3·3	-2·4	4·1
	$\bar{6}$		2·7	-1·0	-2·7	-2·5	-1·3
	$\bar{7}$		1·5	-	-	-1·9	-3·1
	$\bar{8}$		-1·7	-	-1·8	1·1	-2·1
	$\bar{9}$		0·4	0·5	1·3	1·2	0·8
	$\overline{10}$				0·4	0·5	1·3

(h3$\underline{1}$) (k = 3) continued.

		h = 6	7	8	9
	8				
	7				
	6				
	5				
	4				
	3	-			
	2	-	0·7		
	1	-0·5	-1·2		
$\underline{1}$	0	-0·9	-1·4	-0·6	
	$\overline{1}$	-3·6	2·7	-2·7	
	$\overline{2}$	-6·1	4·7	-4·6	1·8
	$\overline{3}$	-7·5	-4·0	-4·6	0·5
	$\overline{4}$	-6·7	-5·2	-4·7	-2·2
	$\overline{5}$	-3·7	3·2	-2·2	-
	$\overline{6}$	-2·7	1·7	-0·9	1·3
	$\overline{7}$	-2·1	-2·4	-	-
	$\overline{8}$	1·3	-1·7	-	-
	$\overline{9}$	2·1	-0·7	-	
	$\overline{10}$	0·8	1·0		

(h4$\underline{1}$) (k = 4)

	h	0	1	2	3	4	5
	8	-					
	7	-	-2·7				
	6	-0·7	-	0·5	-		
	5	-5·4	-1·2	2·4	-	-	
	4	-7·0	-3·3	-1·9	0·9	2·0	0·4
	3	0·9	-3·8	-	-	0·9	0·8
	2	-1·6	-1·8	5·0	-4·4	2·2	-1·8
	1	-3·3	-3·3	-1·5	-4·2	-1·0	-3·7
$\underline{1}$	0	0·8	1·0	-	-	-2·7	-1·5
	$\overline{1}$		5·8	-5·5	5·2	-1·0	1·3
	$\overline{2}$		-3·0	-10·5	-1·8	-9·8	-
	$\overline{3}$		-2·9	-4·5	-8·7	-9·3	-6·0
	$\overline{4}$		6·0	-4·7	1·2	-1·9	-2·7
	$\overline{5}$		4·6	-9·9	6·8	-4·0	2·3
	$\overline{6}$		-1·1	-5·1	-1·4	-5·1	1·0
	$\overline{7}$		-1·0	-	-2·0	-	-1·1
	$\overline{8}$		1·1	-	1·1	-	1·1
	$\overline{9}$			-	1·2	-	0·9

(h4$\underline{1}$) (k = 4) continued.

		h = 6	7	8	9
	8				
	7				
	6				
	5				
	4				
	3				
	2	1·6			
	1	-0·7	-0·7		
$\underline{1}$	0	-2·0	-0·9		
	$\bar{1}$	-1·1	-1·0	-	
	$\bar{2}$	-2·1	-1·1	1·9	
	$\bar{3}$	-5·7	-1·3	1·2	
	$\bar{4}$	-1·1	-1·3	-0·8	-
	$\bar{5}$	2·1	-1·1	1·9	-
	$\bar{6}$	-0·8	-	1·2	-
	$\bar{7}$	-	-	-	
	$\bar{8}$	-	-	-	
	$\bar{9}$	-	-		

(h5$\underline{1}$) (k = 5)

	h	0	1	2	3	4	5	6	7	8	9
	7	-									
	6	-	-								
	5	-	-	3·3	-						
	4	-	0·8	2·8	-	0·4					
	3	1·8	0·7	-	-	-					
	2	6·3	-6·1	-1·9	-0·8	-1·8	0·4				
	1	3·1	-4·6	-	-2·7	-3·6	1·0	-0·8			
$\underline{1}$	0		1·3	-	0·9	-2·5	-1·3	-0·9			
	$\bar{1}$		-3·8	-1·5	1·6	0·9	-1·0	0·8	-		
	$\bar{2}$		-10·2	-6·6	-7·9	0·8	-2·6	3·4	-		
	$\bar{3}$		-3·3	-6·0	-4·3	-2·8	-1·8	2·2	-	-	
	$\bar{4}$		1·0	2·7	1·0	1·1	0·7	0·7	-	-	
	$\bar{5}$		-3·2	3·6	-5·5	5·9	-3·2	1·7	-	-	
	$\bar{6}$		-1·8	1·1	-4·1	2·5	-4·8	1·3	-2·5		
	$\bar{7}$		-	0·7	-	-	-	0·5	-		
	$\bar{8}$			-	-	0·4	1·1	-			

(h6$\underline{l}$) (k = 6)

		h						
		0	1	2	3	4	5	6
	6	-						
	5	-	-					
	4	-	-	1·1				
	3	-1·4	-	-	-			
	2	-7·5	2·4	-4·8	1·8	0·7		
	1	-3·6	2·7	-7·4	2·5	-	0·9	
$\underline{l}$	0	-	-	-1·1	-	-	-	
	$\bar{1}$		-0·9	-	-	1·0	-	-
	$\bar{2}$		-1·7	-3·5	1·3	0·9	2·4	0·4
	$\bar{3}$		-	-0·7	-	-	2·1	0·4
	$\bar{4}$		2·7	-	-0·9	-	-	-
	$\bar{5}$		-0·9	-	-0·8	-2·5	-	-2·0
	$\bar{6}$		-	-	-	-1·7	-	-2·6
	$\bar{7}$				-	-		

(h7$\underline{1}$) (k = 7)

		h				
		0	1	2	3	4
	4	-				
	3	-	-			
	2	-	-	2·3		
	1	-0·7	-1·8	2·1	-2·2	
$\underline{1}$	0		-	0·7	-0·6	
	$\overline{1}$		1·8	1·9	0·7	-
	$\overline{2}$		-	3·2	-	-
	$\overline{3}$		-	1·3	-	1·3
	$\overline{4}$		-	-	-	-

In the zones given above, in Table XI, all possible planes which are within the reciprocal sphere for = 1·54Å. are listed, whether observed or not, i.e. a blank space under any given index will indicate that that plane lies without the reciprocal sphere.

The research involved up to the point of preparing Table XI, in which the magnitudes of the naphthalene structure factors with their appropriate signs were experimentally derived, was carried out in close collaboration with Dr. J. G. White.

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